Macrocyclic compounds derived from Perfluoro-4-isopropylpyridine

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A Thesis Entitled

Macrocyclic Compounds Derived from Perfluoro-4-isopropylpyridine

Submitted by

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Acknowledgements

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Finally I thank my girlfriend Julie for food, drink and transport to the gym.

Memorandum

The work present within this thesis was carried out at the University of Durham between October 1998 and August 2001. This thesis is the work of the author, except where acknowledged by reference and has not been submitted for any other degree. The copyright of this thesis lies solely with the author and no quotation from it should be published without prior written consent and information derived from it should be acknowledged.

Part of this work has been the subject of the following

R. D. Chambers, P. R. Hoskin, A. Kenwright, P. Richmond and G. Sandford, *Arkivoc*, 2000, **1**, 5

and has been presented at:

R.S.C. Fluorine Group Meeting, University of Leicester, September 2001
ACS Pacific Basin Meeting, Hawaii 2001
13th European Symposium on Fluorine Chemistry, Bordeaux 2001
I.C.I. Poster Session, University of Durham, January 2001
Royal Society Perkin Seminar, University of Durham, April 2001

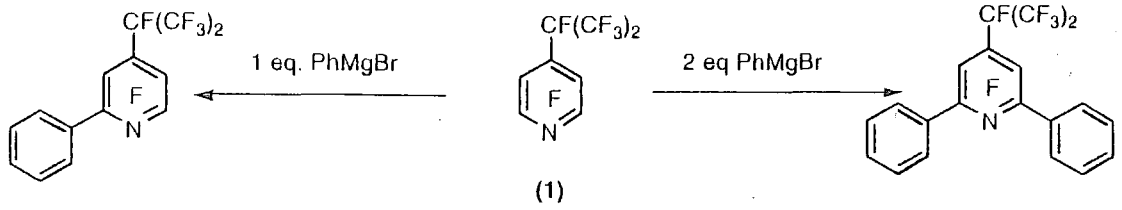
Abbreviations

NMR	Nuclear Magnetic Resonance
IR	Infrared
THF	Tetrahydrofuran
HFP	Hexafluoropropene
TFA	Trifluoroacetic acid
TDAE	Tetrakis(dimethylamino)ethene
TAS-F	Tris(dimethylamino)sulfur(trimethylsily)difluoride

Note that fluorine in the centre of an aromatic ring denotes all of the hydrogen atoms have been replaced by fluorine.

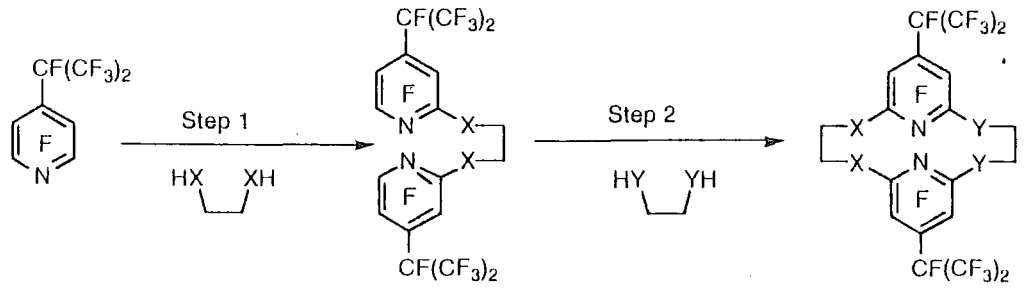
Abstract

Perfluoro-4-isopropylpyridine (1) has been shown to undergo nucleophilic substitution reactions with wide range of nucleophiles and was thus demonstrated to behave as a powerful regioselective electrophile in most cases.



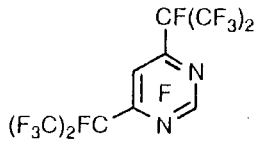
(1)

This work has enabled a series of highly fluorinated macrocyclic compounds to be synthesised based on highly fluorinated pyridine derivatives.

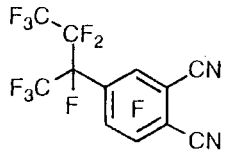


X = NMe, O

Polyfluoroalkylation and nucleophilic substitution in tetrafluoropyrimidine and tetrafluorophthalonitrile give highly fluorinated products that react readily with nucleophiles.



Perfluoroalklyated pyrimidine derivative



Perfluoroalklyated phthalonitrile derivative

Contents

Chapter I Introduction.

1) General Introduction to Organofluorine Chemistry.

Compounds containing carbon bonds to fluorine are extremely rare in nature with only a few examples known and, consequently, organofluorine compounds are almost entirely man-made. This is surprising because fluoride is widespread and has been estimated to be the thirteenth most abundant element within the Earth's crust.[1] Sources of fluorine include mineral deposits such as, fluorspar CaF_2, cryolite $NaAlF_6$ and phosphate rocks, e.g. fluoropatite $CaFCa_4(PO_4)_3$.

The principle source of fluorine for fluorocarbon compounds in industry is anhydrous hydrogen fluoride[2, 3], obtained by distillation from a mixture of fluorspar and concentrated sulfuric acid. Synthesis of organofluorine compounds can then be achieved using a range of techniques including: direct fluorination using elemental fluorine, electrochemical fluorination and reactions with a variety of metal fluorides, of which the most important are those using HF and SbF_5.[4]

Fluorine can impart unique properties into organic systems, arising from the nature of fluorine and its bonds to carbon; several properties are listed below:

1) Fluorine forms the strongest single bond to carbon (485 $kJmol^{-1}$)[5] and enhanced thermal stability to organic compounds is often observed, for example, tetrafluoromethane only undergoes decomposition at temperatures in excess of 2000 °C![6]

2) Fluorine is the most electronegative element,[7, 8] therefore, carbon-fluorine bonds are more polarised and ionic in character than other carbon-halogen bonds.

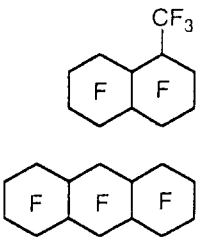
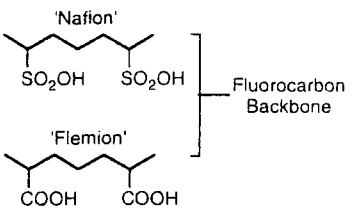
3) Fluorine is the halogen with a Van der Waals radius closest to that of hydrogen (F, 1.47 Å; Cl, 1.75 Å; H, 1.20 Å),[9, 10] therefore, multiple substitution of hydrogen by fluorine is possible without a major disruption to the geometry of a system.

4) Fluorine possesses three tightly bound, non-bonding electron pairs, which results in weak intermolecular interactions between perfluorinated systems, increased volatilities and much lower cohesive energies compared to their hydrocarbon counterparts.[11]

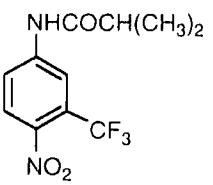
1.1) Applications of Fluorocarbon Compounds.

The unique properties of fluorocarbon compounds, such as enhanced chemical and thermal stability, low surface energies and surface properties and have been utilised for numerous industrial applications[1,2], and some examples are displayed in table 1.

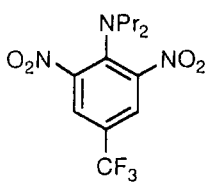
Table 1

Application	Example
Refrigerants	CF_3CH_2F
Inert fluids and heat transfer liquids	
Anaesthetics	$CF_3CHBrCl$ Fluothane™ $CHClFCF_2OCHF_2$ Enflurane™
Polymers	PTFE $-(CF_2CF_2)_n-$ PVDF $-(CH_2CF_2)_n-$
Fluorinated membranes	

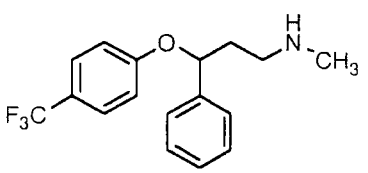
Introduction of fluorocarbon groups into drugs can impart enhanced biological activities on a range of systems and numerous commercial products are available[1,3], several examples are shown.



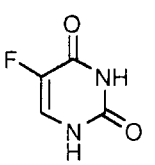
Futamide
Treatment for prostate cancer



Trifluralin
Weed-control in maize



Prozac or Fluoxetine
Anit-depressant



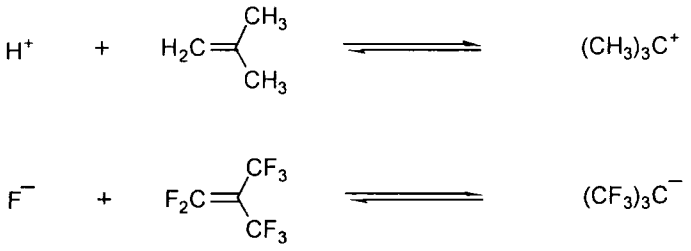
5-fluoro-uracil
Treatment for breast cancer

2) Chemistry of Highly Fluorinated Alkenes.

In this thesis we present the chemistry of some highly fluorinated aromatic and heteroaromatic compounds bearing relatively large perfluoroalkyl groups, which are derived from highly fluorinated aromatic compounds and fluorinated alkenes. Therefore, it is worthwhile discussing some of the aspects that govern the chemistry of fluorinated alkenes. It is a useful starting point as many topics that are important later, such as carbanion stability in fluorocarbon systems, are discussed.

2.1) Introduction.

Highly fluorinated alkenes are electron deficient species and are consequently susceptible to nucleophilic attack.[14] There is therefore, essentially, a 'mirror-image' relationship between the chemistry of alkenes and that of highly fluorinated alkenes, in that the former can undergo electrophilic reactions with H^+ to produce carbocations and the latter can undergo nucleophilic reactions with F^- to produce carbanions.

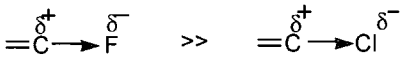


The regio-chemistry of nucleophilic attack on fluorinated alkenes can be attributed to several factors, including, inductive effects and carbanion stability in fluorinated systems, which will now be discussed.

2.2) Factors Affecting Nucleophilic Attack.

2.2.1) Inductive Effect.

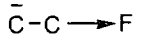
As already mentioned, fluorinated alkenes are susceptible to nucleophilic attack and this can be attributed to the inductive effect of fluorine in a carbon-fluorine bond.[15] This gives rise to a significant ion-dipole interaction that contributes greatly to the increased reactivity of alkenes bearing fluorine substitutents over that of chlorine, because the inductive effect of fluorine is far greater than that of chlorine.[16]



2.2.2) Stability of Fluorinated Carbanions.

The stability of the carbanion intermediates is significant in determining the reactivity and regioselectivity of nucleophilic attack in fluorinated alkenes and factors influencing carbanion stability in fluorocarbon systems will now be considered.

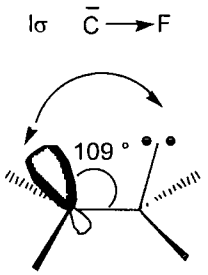
Fluorine attached to a carbon atom adjacent to the carbanion site is highly carbanion stabilising due to Iσ electron-withdrawing effects.[17, 18]



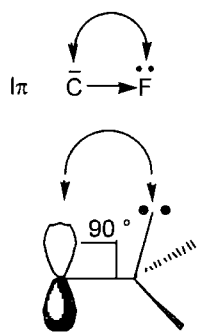
Highly Stabilising

However, for a fluorine atom attached directly to the carbanion centre there are two opposing effects to consider, Iσ and electron pair repulsion Iπ, the resultant of these effects is dependent on the geometry of the system.

It has been established that the Iπ repulsion effect is greater for a planar sp^2 hybridised carbanion than if the carbon is tetrahedral.



sp^3 hydbridised system
Stabilising



sp^2 hydbridised system
Destabilising

Consequently, for sp^2-hybridised systems the Iπ destabilising effect dominates over the Iσ stabilising effect and is overall destabilising, whereas, for sp^3-hybridised systems the Iσ effect dominates and is overall stabilising.

Understanding the effects which govern carbanion stability can be used to explain the reactivity series of the fluorinated alkenes shown below;

$$F_2C{=}CF_2 \quad > \quad F_2C{=}CFCF_3 \quad > \quad F_2C{=}C(CF_3)_2$$

Increasing Reactivity

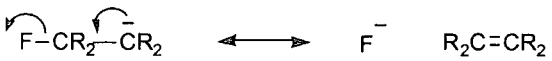
In each case nucleophilic attack occurs at the difluoromethylene site, producing the following carbanion intermediates;

$$Nuc{-}CF_2{-}\bar{C}F_2 \quad > \quad Nuc{-}CF_2{-}\bar{C}FCF_3 \quad > \quad Nuc{-}CF_2{-}\bar{C}(CF_3)_2$$

Increasing Stability

This series thus demonstrates the greater carbanion stabilising effect for a fluorocarbon group than for fluorine itself, because, there is an increase in carbanion stability when a fluorine atom is replaced by a fluorocarbon group at the carbanion centre.

However, in 1950, Roberts suggested an additional carbanion stabilising effect involving the concept of negative-hyperconjugation, or non-bond resonance in fluorocarbon systems.[19, 20]

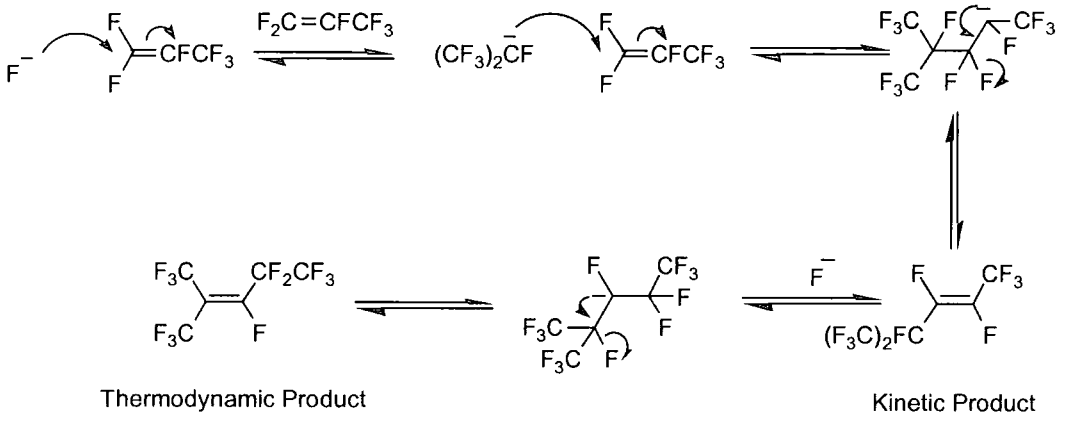


Although there is notable evidence suggesting that this phenomenon occurs, there is no real explanation of how significant it is in relation to kinetic data for reactions of such systems,[21] and therefore, negative hyperconjugation is still the subject of debate.

We now have a series of ground-rules regarding carbanion stability in fluorocarbon systems and this information will be referred to later, when we discuss the chemistry of highly fluorinated heteroaromatic compounds. At present they provide a useful tool in understanding the chemistry of fluorinated alkenes and a particularly good example to illustrate this chemistry is the reaction of hexafluoropropene with fluoride ion, which will now be considered.

2.3) Reactions of Fluorinated Alkenes.

In general fluorinated alkenes undergo nucleophilic attack by range of nucleophiles and this has led to a series of addition, elimination and rearrangement reactions. The reactions of fluorinated alkenes with fluoride ion are especially relevant to this work. For example, hexafluoropropene (HFP) reacts with fluoride ion to generate a carbanion, and this carbanion can then react as a nucleophile with another molecule of HFP to give a kinetic and a thermodynamic product.



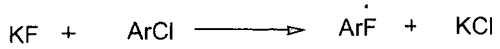
Reaction of the kinetic product with additional fluoride ion results in conversion to the thermodynamic isomer; this is a fluoride-ion-induced rearrangement and several good examples highlight the diverse nature of this chemistry.[22-24]

Thus we can see that fluorocarbanions derived from fluoroalkenes can behave as nucleophiles and several reactions have been documented.[25] Perhaps the most interesting aspect of this chemistry are the so-called negative Friedel-Crafts reactions, involving the reactions of fluorinated alkenes and highly fluorinated aromatic compounds. However, an understanding of highly fluorinated aromatic compounds is necessary before we consider negative Friedel-Crafts reactions. Therefore, we turn our attention to the chemistry of fluorinated heteroaromatic compounds, looking at the synthesis of such compounds, the mechanistic aspects of their reactions and indeed a further examination of their chemistry, including that of negative Friedel-Crafts reactions.

3) Chemistry of Highly Fluorinated Heteroaromatic Compounds.

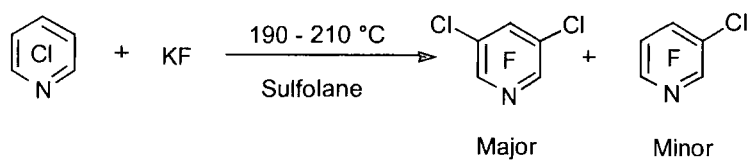
3.1) Synthesis.

Although many different routes to highly fluorinated aromatic systems are known[26-28], perhaps the most practical method involves the nucleophilic displacement of chlorine by fluorine, using alkali metal fluorides.

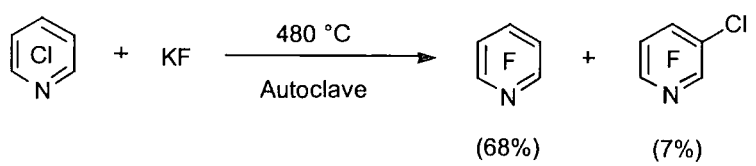


The reactivity of the alkali metal fluorides decreases in the series CsF > KF >> NaF (i.e. as the lattice energy increases) and because the nucleophilicity of fluorine decreases substantially on solvation, dipolar aprotic solvents are often required. The use of crown-ethers with potassium fluoride has been documented to overcome solubility difficulties and increase the reactivity of fluoride, producing so-called 'naked-fluoride-ion'.[29-31]

The reaction of pentachloropyridine with potassium fluoride in sulfolane produces a mixture of two fluorinated products.[32]



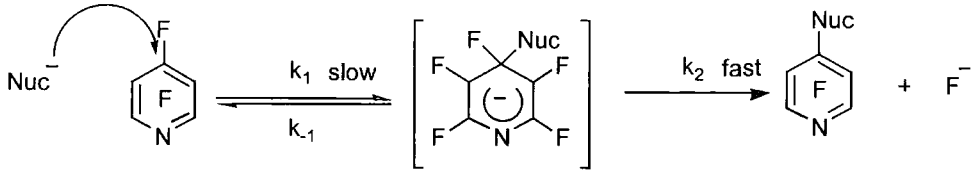
However, further fluorination under these conditions is limited by the thermal stability of the solvent. One way of overcoming this problem is to eliminate the solvent from the reaction, and autoclaves have been used to achieve this at high temperatures. For example, Chambers and co-workers have developed an efficient route to pentafluoropyridine using potassium fluoride and pentachloropyridine, in the absence of solvent at 480 °C.[32, 33]



Numerous highly fluorinated heteroaromatic compounds have been made in a similar manner and for a table of reagents and conditions the reader is directed to the literature.[34]

3.2) Nucleophilic Aromatic Substitution Reactions in Highly Fluorinated Aromatic Compounds.

Highly fluorinated aromatic compounds generally undergo nucleophilic substitution reactions, and it is a reasonable assumption that displacement of fluoride from a highly fluorinated aromatic system proceeds via a two-step mechanism.[35] In this mechanism the nucleophilic species is bonded to the aromatic system before fluoride is displaced and it is the first step which is rate-limiting.

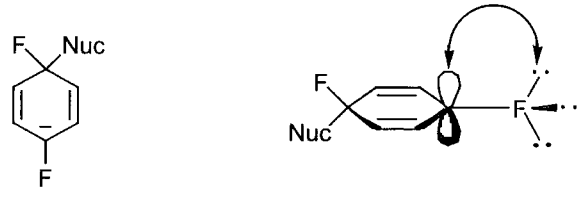


An example of nucleophilic aromatic substitution in pentafluoropyridine showing the two-step process via the transition state.

The fact that fluoride is the most reactive of all the halogens in such reactions suggests that the rate-limiting step involves little C-F bond breaking.[36]

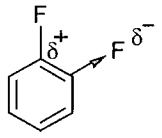
Kinetic data for substitution reactions in various fluoroaromatic compounds have concluded that *ortho-* and *meta-* fluorines are both activating with respect to hydrogen, whereas a *para-* fluorine is slightly deactivating to nucleophilic attack. The electron distribution at the transition-state can help explain the observed substitution patterns in highly fluorinated aromatic species and we shall consider the effect of each fluorine in turn, *ortho-*, *meta-* and *para-* to the site of attack.[37-40]

We have already discussed some of the factors that influence carbanion stability in fluorocarbon compounds and we stated that a fluorine atom directly attached to a planer sp^2-hybridised carbanion centre is slightly destabilising with respect to hydrogen.



Iπ replusion dominates

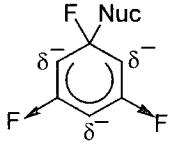
In the case of a fluorine atom *para-* to the site of attack, delocalisation of charge would be destabilising at this site. The same effect would be expected for the *ortho-* fluorines, however, it has been suggested that the activating effect of *ortho-* fluorine atoms is due to a large polar influence that is strongly activating in the initial state and is the dominant influence at this site.

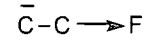


Activating effect by *ortho-* fluorine
Enhances the electrohpilic character o
the C-F bond under attack

There is evidence to support this view because; the influence of *ortho-* relative to *meta-* fluorines increases with the reactivity of the system (see below).

The activating influence of a *meta-* fluorine is easier to explain, in that the charge is delocalised adjacent to the carbon fluorine bond at the *meta-* site and is therefore strongly stabilising.





Highly Stabilising

Activating effect by *meta-* fluorine

Therefore, it is correct to say that, nucleophilic attack in highly fluorinated aromatic compounds occurs so as to minimise the number of *para-* fluorine atoms and thus maximise the number of activating *ortho-* and *meta-* fluorine atoms.

Although both *meta-* and *ortho-* fluorines are activating, the extent to which each contributes is dependent on the system. For example, in hexafluorobenzene the *meta-* fluorines are more activating than the *ortho-* fluorines, whereas in the more reactive pentafluoropyridine system the *ortho-* fluorines are more activating. This is further evidence for the activating effect of the *ortho-* fluorine atoms in the initial state. For a more reactive system the transition-state will more closely resemble the starting materials, thus the inductive effect of the *ortho-* fluorines at an earlier transition-state is more significantly activating than the *meta-* fluorines. However, in the less reactive

system the transition-state is more product-like and the *meta-* fluorines are found to be more activating.

3.3) Pentafluoropyridine.

As mentioned above, pentafluoropyridine is a more reactive system than hexafluorobenzene, due to the activating effect of ring nitrogen. Indeed the dominating effect of nitrogen is highlighted by the enormous reactivity increases along the series of perfluorinated derivatives of benzene, pyridine, pyrimidine and triazine.[34]

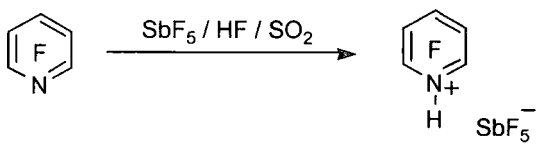
In the case of pentafluoropyridine, nitrogen would be expected to direct substitution *ortho-* and *para-*, however, it is found that nucleophilic substitution is, with few exceptions, exclusive to the 4-position, that is, *para-* to nitrogen. This has been explained by the powerful electron-withdrawing effects of the fluorines *ortho-* to the site of attack and a comparison of the positions of attack in 2,4,6-trifluoropyridine and pentafluoropyridine provides evidence that the *ortho-* fluorines form an additional orienting effect.[41-43]

(4: 78%)
(2: 22%)

(4: 100%)

Positions of substitution by aqueous NH_3

Another effect of the ring fluorine atoms in pentafluoropyridine, is their influence on base strength. The electron-withdrawing effects of the two fluorines *ortho-* to nitrogen render pentafluoropyridine almost entirely non-basic, and salts are only formed with extremely powerful acids.[44]

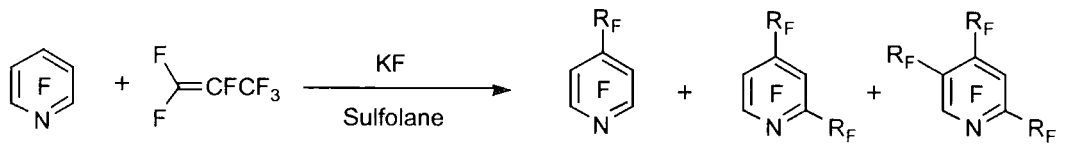


The reactions of pentafluoropyridine with a range of oxygen, carbon, nitrogen and sulfur-centred nucleophiles has been reviewed[45] and such reactions are important in this work. However, we shall first consider the introduction of a perfluoroalkyl group into pentafluoropyridine using HFP, as this leads to the synthesis of perfluoro-4-isoproplypyridine, which provides the starting point in this study. We will examine the

aspects and practicalities of this reaction before looking at some further nucleophilic substitution reactions.

3.4) Perfluoroalkylation.

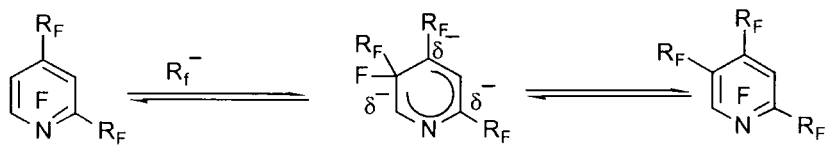
A reaction between pentafluoropyridine and a fluorocarbanion generated from the reaction of fluoride ion with HFP gives rise to mono-, di-, and tri-substituted products.[46]



$R_F = CF(CF_3)_2$

Polysubstitution raises some interesting issues:

i) After two polyfluoroalkyl groups are present they can direct the position of further substitution. This is because the highly electron-withdrawing perfluoroalkyl groups at the 4- and 6-positions in **(2)** can stabilise the carbanion intermediate in the transition-state **(2a)** and this effect dominates over the influence of ring nitrogen in this situation.



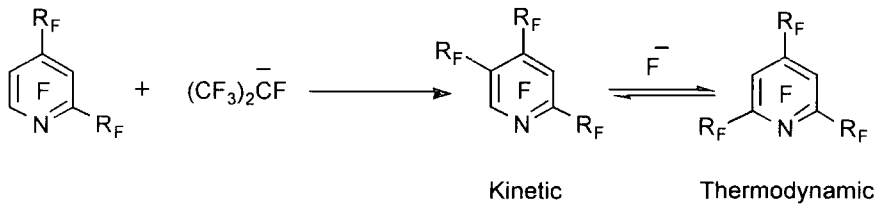
(2) **(2a)**

$R_F = (CF_3)_2CF$

ii) Some of the reactions are reversible and can undergo fluoride-ion-induced rearrangements.

iii) Substitution at the most activated site can lead to steric crowding, giving a product that is not the most thermodynamically stable isomer. There is therefore, competition between kinetic and thermodynamic products.

These factors are all exemplified by the substitution of a third perfluoroalkyl group into the pentafluoropyridine derivative shown below.



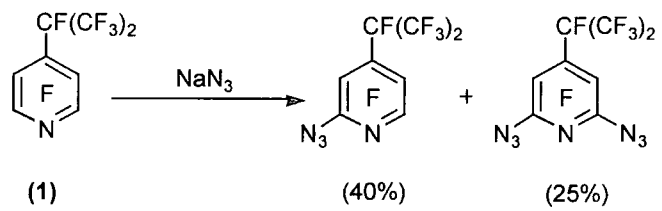
$R_F = CF(CF_3)_2$

In the kinetic product, substitution is directed by the two highly activating perfluoroalkyl groups, however, this leads to a sterically demanding product. Fluoride-ion-induced rearrangement of the kinetic isomer highlights the reversible nature of the reaction and leads to the most thermodynamically stable 2,4,6-trisubstituted product.[47]

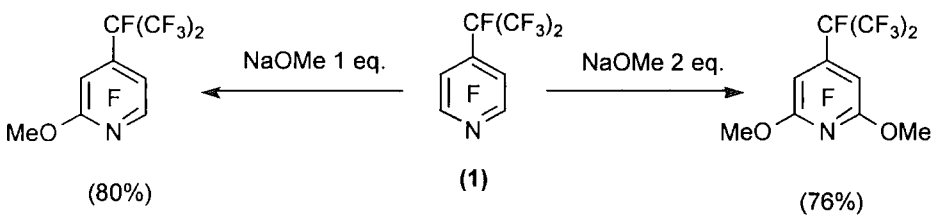
3.4.1) Nucleophilic Substitution Reactions in Perfluoro-4-isopropylpyridine.

Until recently, the chemistry of perfluoro-4-isopropylpyridine **(1)** has been largely unexplored, however, several reactions have been reported.

Banks has reported the synthesis of azide derivatives of **(1)**.[48]



Also, Chambers and Haszeldine have independently shown that **(1)** reacts with methoxide ion to give mono- and di-substituted products.[49, 50]



Temperature dependant conformational isomers of **(1)** have been observed by ^{19}F NMR techniques.[50]

Chapter II Nucleophilic Aromatic Substitution in Perfluoro-4-isopropylpyridine.

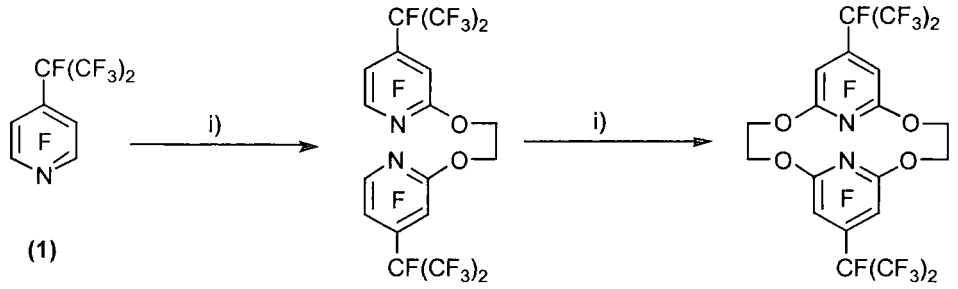
1) Introduction.

In this chapter we will explore the chemistry of perfluoro-4-isopropylpyridine (1). Previous work with perfluoro-4-isopropylpyridine (1) has been severally limited by the difficulty in isolating (1) from the reaction media. Sources of fluoride ion for the perfluoroalkylation reactions used are alkali metal fluorides, such as potassium fluoride, but, isolation of the products from the dipolar aprotic solvents required for such reactions, results in low overall yields.[46] However, improved methodology (see below) has since been developed which negates the need for a solvent and has provided an excellent route to perfluoroalkylated heteroaromatic compounds, allowing scale-up of the reaction. This methodology has allowed Chambers and co-workers to fully explore the chemistry of perfluoro-4-isopropylpyridine for the first time.

More recently in these laboratories, Hoskin[51] has investigated the chemistry of (1) through a series of nucleophilic aromatic substitution reactions. This work was fundamental in demonstrating that (1) behaves as a powerful electrophile and nucleophilic substitution could readily be achieved at the 2- and 6-positions with a wide range of reagents, such as alkoxide ions.

Expanding on this work, in preliminary studies, Hoskin was able to produce a highly fluorinated macrocyclic compound based on (1).

E.g.



i) CsF / $TMSOCH_2CH_2OTMS$ / Monoglyme

We aimed to carry out reactions of (1) using a series of nucleophilic aromatic substitution reactions and examine such aspects as: position of substitution by a nucleophile, the directing effects of additional substituents and the robustness of the perfluoroalkyl group.

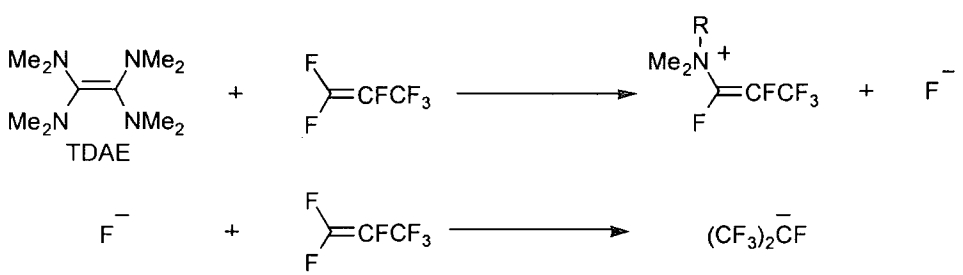
For example, the perfluoroalkyl group has a significant effect on the reactivity and regiochemistry in **(1)**, and in principle could be a leaving group in some reactions. Also we wish to investigate the further reactivity of **(1)** by producing highly substituted pyridine systems.

Whereas previous work has focused on reactions of **(1)** with oxygen nucleophiles to give mono- and di-substituted derivatives, our approach was to expand on this work and examine some tri-alkoxy substituted compounds before looking at a series of both carbon and nitrogen-centred nucleophiles. Reactions of **(1)** with alkoxide ions to give tri-substituted products are examined first, before a series of sp^3, sp^2 and sp-hybridised carbon-centred nucleophiles are discussed. The chapter concludes with an investigation of the reactions of **(1)** with nitrogen-centred nucleophiles.

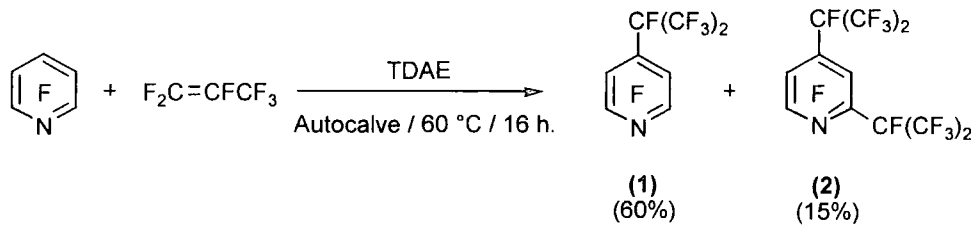
2) Synthesis of Perfluoro-4-isopropylpyridine.

Using tetrakis(dimethylamino)ethene (TDAE) as a catalyst, Chambers and co-workers have developed an effective route to perfluoroalkylated heteroaromatics in the absence of solvent.[52]

TDAE is a good nucleophile and reacts with highly fluorinated alkenes to produce fluoride salts. Under anhydrous reaction conditions, TDAE reacts with HFP producing an 'in situ' source of fluoride ion, which can react with more HFP to give the nucleophilic fluorocarbanion, $(CF_3)_2CF^-$.



This carbanion can then be trapped using pentafluoropyridine, and by careful control of the stoichometry of reagents, perfluoro-4-isopropylpyrdine **(1)** can be produced in excellent yields. Isolation of products is made simple by distillation from the reaction mixture, therefore, perfluoro-4-isopropylpyridine was made on a large-scale (200 g) in good yield, and this provided the main feedstock of **(1)** for this study.

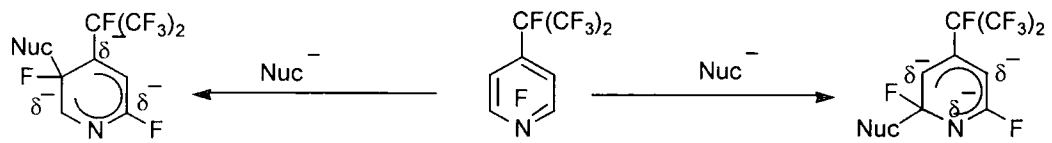


Both **(1)** and **(2)** are colourless liquids (bp, 129 and 139 °C, respectively) and were obtained directly from the crude reaction mixture by careful distillation at atmospheric pressure. Physical and spectral data for **(1)** is available in the literature[46, 47, 50, 52], however, a particularly important feature in **(1)** is the rotation of the perfluoroisopropyl group, which clearly affects the ^{19}F NMR spectrum. **(1)** demonstrates very broad signals for the 2,6- and 3,5-fluorine atoms in the ring, caused by rotation of the perfluoroisopropyl group at room temperature, which is relatively 'slow' on the NMR time-scale.

3) Reactions of (1) with Oxygen Nucleophiles.

3.1) Sodium Methoxide and -Phenoxide.

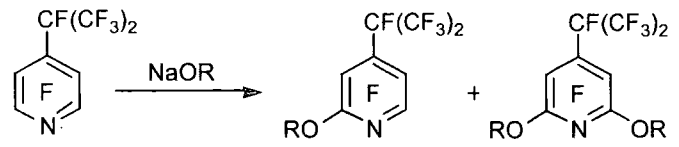
In principle, attack by a nucleophile in **(1)** could occur at either the 2-position, *ortho-* to nitrogen, or at the 3-position, adjacent to the perfluoroalkyl group. In both of these positions of attack, the carbanion intermediates in the transition-state have groups which could stabilise a negative charge.



Attack at 3-position
Charge stabilised by perfluoroalkyl group

Attack at 2-position
Charge stabilised by ring nitrogen atom

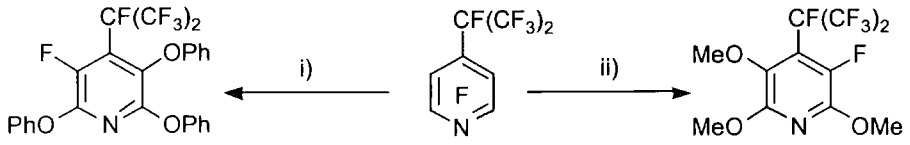
However, for the reactions of **(1)** with a series of alkoxide ions, substitution of fluorine by alkoxide was consistently observed at the 2- and 6-positions to give mono- and di-substituted products. However, no further substitution was observed at the 3- and 5-positions.



(1)

Our approach was to react **(1)** with an excess of alkoxide in order to probe the further reactivity of the system.

A reaction between **(1)** and an excess of sodium methoxide/phenoxide gave the tri-substituted products **(3)** and **(4)** respectively.

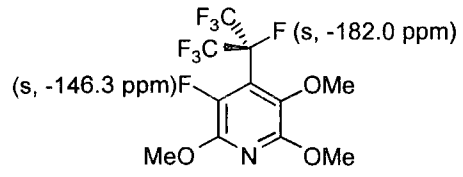


(4) (27%) **(1)** **(3)** (75%)

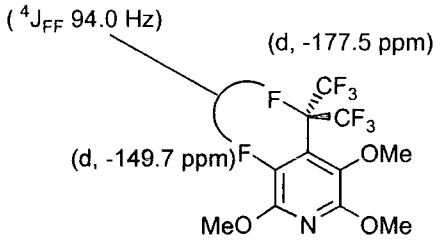
i) NaOPh / THF / 70 °C / 72 h.
ii) NaOMe / MeOH / 70 °C / 72 h.

Introduction of a third alkoxy group is confirmed by ^{19}F NMR spectroscopy and demonstrates the relatively high activating effects of the *ortho-* perfluoroalkyl group and the fluorine *meta-* to the site of attack, which dominate over the destabilising influence of an alkoxy group *para-* to the site of attack.

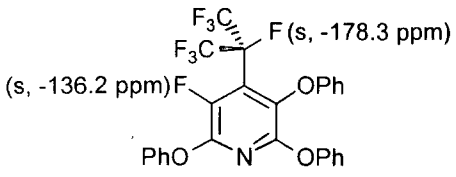
The presence of a ring substituent adjacent to the perfluoroisopropyl group has a considerable effect on the free rotation of this sterically demanding substituent. As mentioned above, rotation of the perfluoroisopropyl group in **(1)** gives rise to broad signals for the 2,6- and 3,5-fluorines. However, in **(3)** and **(4)**, the introduction of a group at the 3-position significantly hinders rotation of the perfluoroisopropyl group and separate conformations are observed by ^{19}F NMR spectroscopy. Two, conformations can be envisaged.



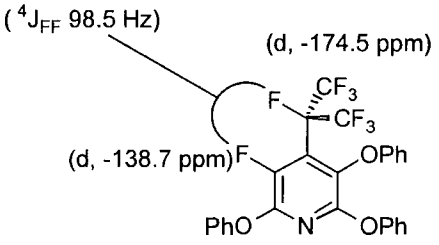
(3)
Conformation A



(3)
Conformation B



(4)
Conformation A



(4)
Conformation B

Figures in parentheses denote multiplicity and chemical shift in the ^{19}F NMR spectrum

Conformation A, in both **(3)** and **(4)** shows the tertiary fluorine of the perfluoroisopropyl group to be distant from the 5-fluorine of the ring, and all of these fluorine atoms are observed as singlets in the ^{19}F NMR spectrum. In the ^{19}F NMR spectrum of conformation B, the 5-fluorine of the ring is shifted to lower frequency, whereas the tertiary fluorine of the isopropyl group is shifted to higher frequency relative to the corresponding signals in conformation A. Conformation B allows the tertiary fluorine of the perfluoroisopropyl group and the 5-fluorine of the aromatic ring to be in a conformation that gives rise to a large through-space coupling (~95 Hz) between these two atoms which is observed in both **(3)** and **(4)**. This coupling constant of is a similar magnitude to that proposed in by Tiddy in similar compounds.[50]

3.2) Calculation of Activation Barriers to Rotation.

As each conformation of the same compound has a significantly different ^{19}F NMR spectrum it was possible to further investigate the nature of rotation of the perfluoroisopropyl group. In the next section we describe how ^{19}F NMR spin-saturation-transfer experiments were used to calculate the activation energy of the barrier to rotation of the perfluoroisopropyl group in **(1)**, **(3)** and **(4)**.

Spin-saturation-transfer is a technique in which physical properties of a molecule can be investigated by NMR spectroscopy. If a molecule contains an exchanging pair of atoms, which give two different signals in the NMR spectrum, then the rate of exchange between those atoms can be determined. For example, compound **(3)** has two possible conformations, A and B, for the tertiary fluorine atom of the perfluoroisopropyl group, and each corresponds to a different resonance in the ^{19}F NMR spectrum. However, because rotation of the perfluoroisopropyl group allows exchange between the two conformations, the two signals are said to be in mutual exchange, that is they are an exchangeable pair. In the case of **(3)** exchange is governed by rotation of the perfluoroisopropyl group and one rotation results in exchange between the signal corresponding to the tertiary fluorine in conformer A and the signal corresponding to the tertiary fluorine in conformer B.

Spin-saturation-transfer is carried out by irradiating one of the two signals of an exchangeable pair with a saturating radio frequency so as to eliminate the signal from the NMR spectrum. However, because this signal was in mutual exchange with the partner atom, some of the saturating radio frequency is transferred, and this signal is also diminished. The extent to which it is diminished is dependent on the rate of exchange between the mutual pair; in the case of **(3)** and **(4)** this is exactly proportional to the rate of rotation of the perfluoroisopropyl group.

Spin-saturation transfer experiments were performed according to the literature[53] on compounds **(1)**, **(3)** and **(4)**. Irradiation of the signal corresponding to the tertiary fluorine atom of the perfluoroisopropyl group of conformer A resulted in a partial loss of intensity for the signal corresponding to conformer B. The experiment was repeated over a temperature range (-50 to +22 °C) and the percentage loss of signal recorded in each case. Rotation of the perfluoroisopropyl group was assumed to be first order and the equation below was used to calculate the rate constant for rotation of the perfluoroisopropyl group at each temperature.

$$k = \frac{1}{T}\left(\frac{M_{Ao}}{M_A} - 1\right)$$

k = rate constant s^{-1}

T = temperature K

M_{Ao} = intensity of signal before irradiation

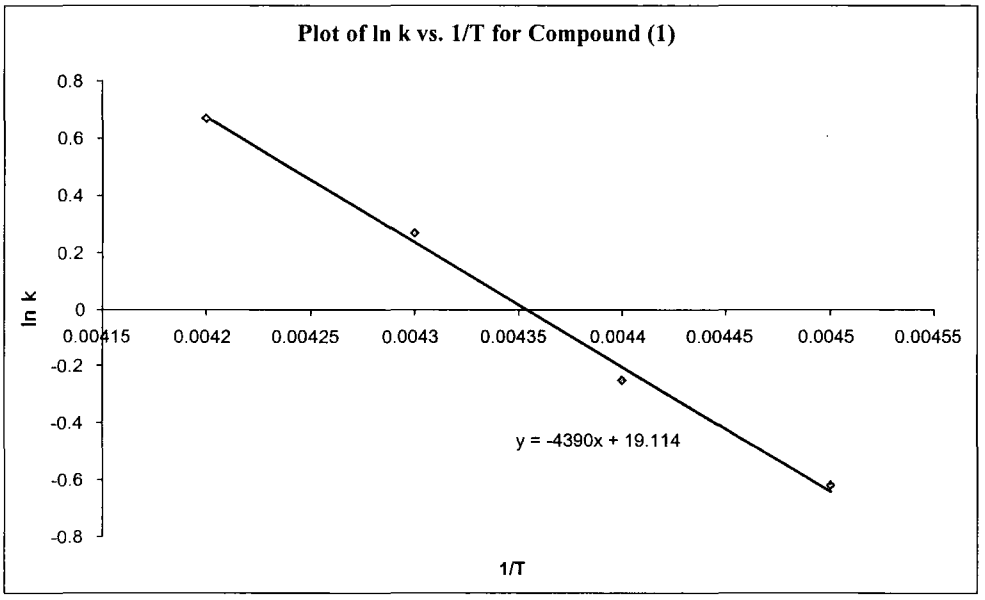
M_A = intensity of signal after irradiation

A plot of $I_n k$ vs. 1/T gave a straight-line graph of gradient $-E_A/R$, where E_A is the activation energy of the barrier to rotation of the perfluoroisopropyl group and R is the gas constant. The results for compounds **(1)**, **(4)** and **(3)** are detailed below.

1) Perfluoro-4-isopropylpyridine

$E_A = 35.7\ kJmol^{-1}$

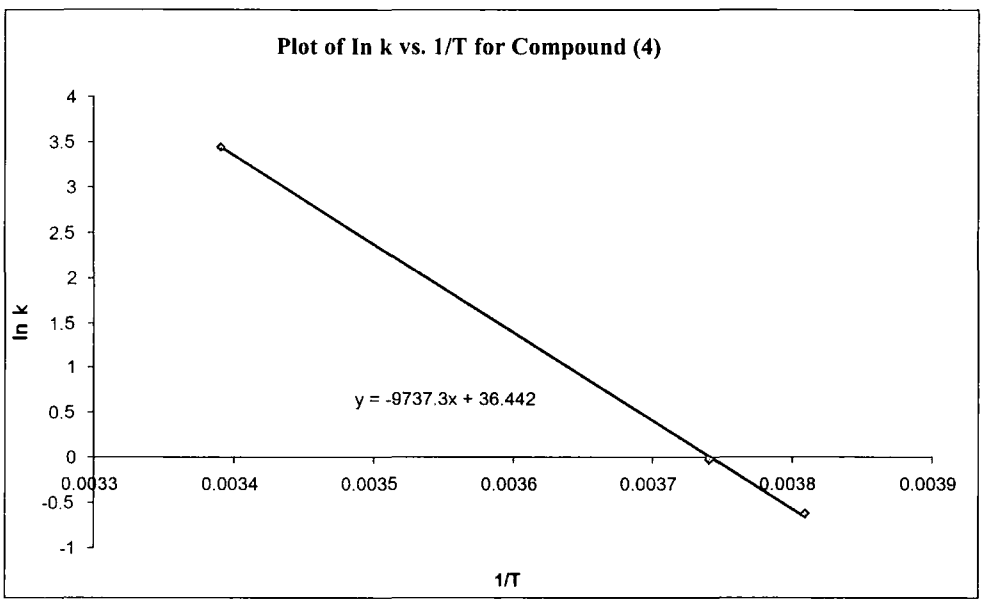
Temp / K	% Loss on Saturation	k / s^{-1}	1/T ($x10^{-3}$)	ln k
236	65	1.95	4.24	0.67
233	52	1.31	4.29	0.27
228	39	0.78	4.39	-0.25
224	28	0.54	4.46	-0.62



(4) 3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine.

E_A = 81.0 kJmol^{-1}

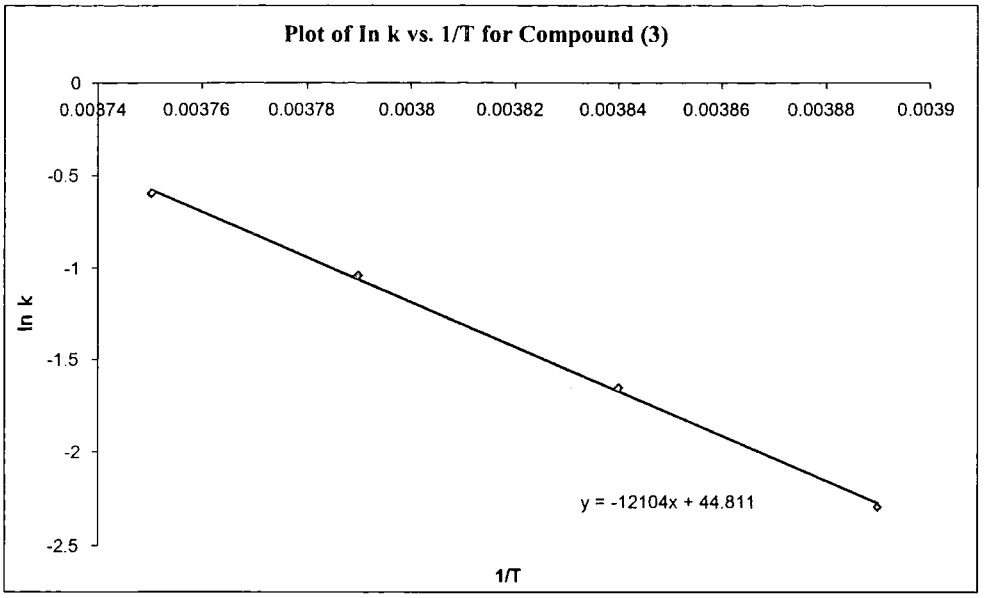
Temp / K	% Loss on Saturation	k / s^{-1}	1/T (x10^{-3})	ln k
295	99	31.2	3.39	3.44
267	59	0.98	3.74	-0.20
263	43	0.54	3.81	-0.62
257	38	0.47	3.89	-0.76



(3) 3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine.

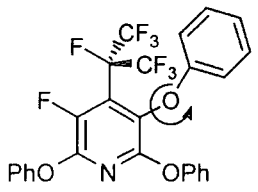
E_A = 100.6 kJmol^{-1}

Temp / K	% Loss on Saturation	k / s^{-1}	1/T (x10^{-3})	ln k
267	52	0.55	3.75	-0.60
264	38	0.35	3.79	-1.04
261	23	0.19	3.84	-1.65
257	13	0.10	3.89	-2.29

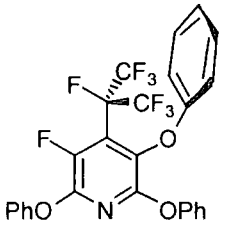


Therefore, in each case the activation to the barrier to rotation of the perfluoroisopropyl group was calculated using Arrhenius parameters, giving values of 35.7, 81.0 and 100.6 $kJmol^{-1}$ for compounds **(1)**, **(4)** and **(3)** respectively.

Thus compound **(1)** has the lowest activation energy for the barrier to rotation of the perfluoroisopropyl group, demonstrating the far lower steric requirement of a fluorine atom than of either phenoxy or methoxy at the same position. The higher barrier to rotation observed for **(3)** over **(4)** might be explained by considering the effects of rotation about the carbon-oxygen bond in both compounds. Whereas in **(3)** a rotation of the methyl group at the 5-position does not alter the steric requirement of this group, the same rotation in compound **(4)** results in the phenyl group being in one of two conformations. For conformation **(4a)** the phenyl group has a significant interaction with the perfluoroisopropyl group, however, in conformation **(4b)** the phenyl group is orthogonal to the pyridine ring and a low steric interaction can be envisaged, allowing the perfluoroisopropyl group to rotate more freely than in **(4a)**.



(4)
Conformation 4a



(4)
Conformation 4b

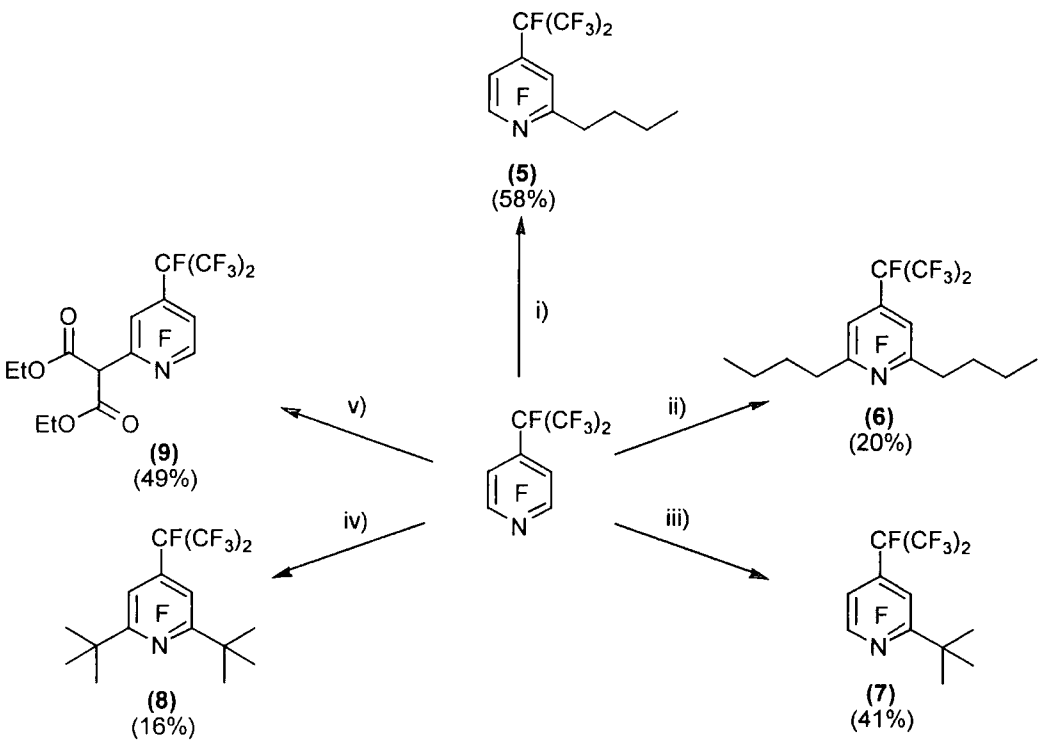
In this section we have described the first synthesis of tri-alkoxy derivatives of **(1)** demonstrating the further reactivity of **(1)** to nucleophilic substitution. These derivatives have been used in the calculation of the activation energy for the barrier to rotation of the perfluoroisopropyl group.

4) Reactions of (1) with Carbon-Centred Nucleophiles.

Pentafluoropyridine has been shown to react with a range of carbon-centred nucleophiles, but, there are no such reported reactions involving **(1)** with carbon-centred nucleophiles. Carbon-centred nucleophiles can have different hybridisation at nucleophilic carbon and therefore, our approach was to investigate the reactions of **(1)** with a series of sp^3, sp^2 and sp-hybridised carbon-centred nucleophiles in turn. The work presented here concentrates on lithium, sodium, magnesium and copper reagents.

4.1) sp^3-Hybridised.

Reactions of **(1)** with a series of sp^3-hybridised carbon-centred nucleophiles gave mono- and di-substituted derivatives, the distribution of products being dependent on the stoichometry of the reagents. The reactions and products are summarised in scheme 1.



Reagents and Conditions

i) BuLi 1eq. / Ether / -78 °C / 45 min. ii) BuLi 2 eq. / Ether / -78 °C / 45 min. iii) ^{t}BuMgCl / THF / -15 °C / 5 h. iv) ^{t}BuLi / CuBr / Ether / -40 °C / 6 h. V) Diethylmalonate / NaH / THF / 0 °C / 6h.

(Scheme 1)

In each case nucleophilic substitution occurs at the 2- and 6-positions only and this is consistent with previous work involving oxygen nucleophiles. The ^{19}F NMR spectrum of pentafluoropyridine clearly shows large a difference in value for 3,5- and the 2,4,6-fluorine sites, and the substituent induced chemical shifts arising from replacement of a 2- or 4-fluorine atom are usually small in comparison with the chemical shift differences in pentafluoropyridine. Therefore, we are able to clearly distinguish between the 2,6- and 3,5-fluorine atoms in (**1**), and consequently, the replacement of the 2,6-fluorine atoms rather than the 3,5-fluorine atoms is evident. Introduction of two nucleophiles into (**1**) gives rise to a symmetrical product and one signal for the 3- and 5-fluorines is generally observed in the ^{19}F NMR spectrum. If substitution had occurred at the 3- or 5-positions the molecule would of course no longer be symmetrical and a more complex pattern would be observed, and this is clearly not the case here.

Reaction of (**1**) with one equivalent of butyllithium resulted in nucleophilic substitution of fluorine by butyl anion giving compound (**5**) in good yield, but, substitution of a second butyl group using butyllithium was less efficient, giving compound (**6**) in low yield.

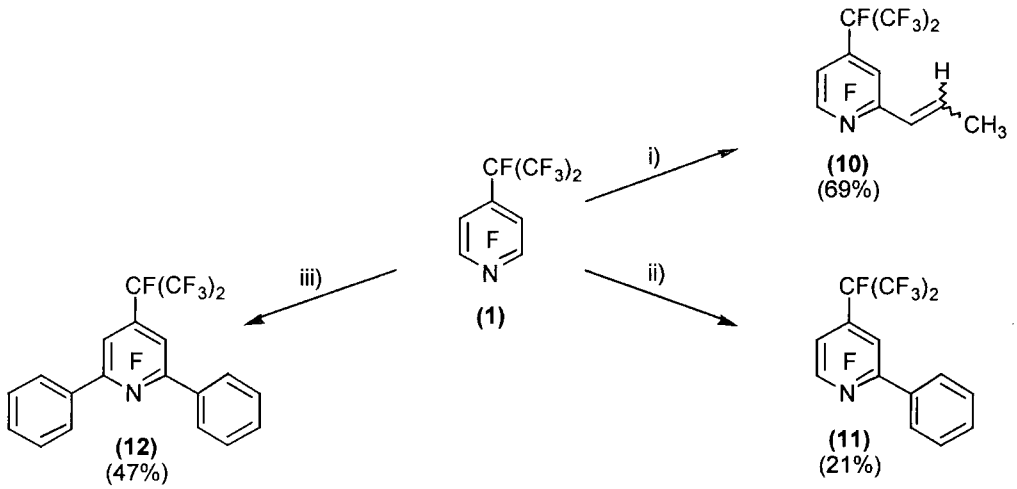
Attempts to introduce a tertiary-butyl group into (**1**) using tertiary-butyllithium were unsuccessful, giving complex mixtures of products in all cases. Nevertheless, introduction of one tertiary-butyl group was achieved using tertiary-butylmagnesium chloride in THF, giving compound (**7**) in fair yield. A reaction of (**1**) with two equivalents of tertiary-butylmagnesium chloride did not result in further substitution. Introduction of two tertiary-butyl groups was eventually achieved using an alkyl copper reagent generated from mixture of Cu(I)Br and tertiary-butyllithium at low temperature.[54] Even so, this method only gave compound (**8**) in low yield and unfortunately all attempts to improve the yield were unsuccessful.

The abstraction of a proton from diethylmalonate using sodium hydride to produce an enolate anion was effective and reaction of this anion with (**1**) afforded compound (**9**) in good yield. Further nucleophilic substitution was not attempted.

In this series we have examined the reactions of (**1**) with sp^3-hybridised carbon-centred nucleophiles using a variety of reagents. In all cases substitution was observed at the 2- and 6-positions, further demonstrating the efficacy of (**1**) as a di-functional, regioselective electrophile.

4.2) sp^2-Hybridised.

The reactions of **(1)** with a series of sp^2-hybridised carbon-centred nucleophiles are summarised in scheme 2.



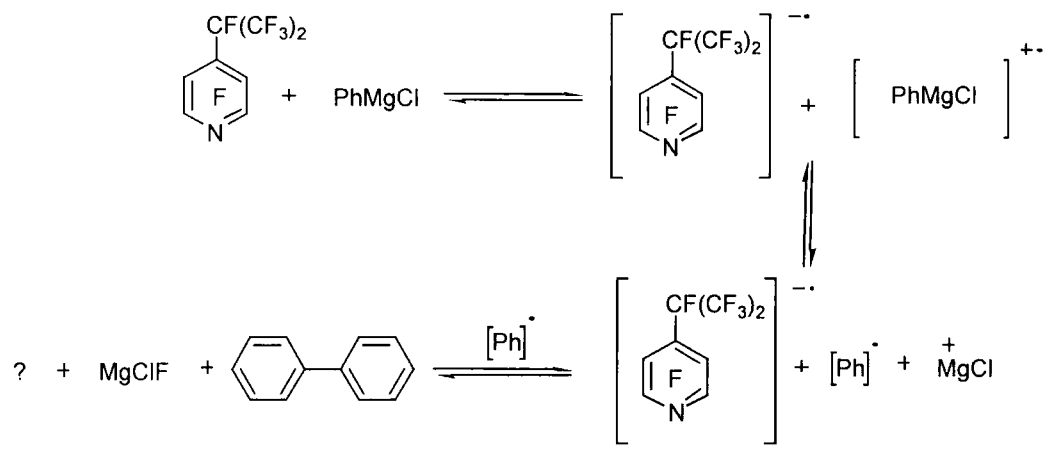
Reagents and Conditions
i) 1-propenylmagnesium bromide / THF / 65 °C / 20 h. ii) Phenylmagnesium chloride / THF / 65 °C / 1 d.
iii) Phenylmagnesium bromide / THF / 65 °C / 20 h.

(Scheme 2)

Reaction of **(1)** with 1-propenylmagnesium bromide gave compound **(10)** in good yield and substitution occurred at the 6-position in a manner consistent with previous work in this series.

The ^{1}H NMR spectrum of **(10)** shows the presence of both *E* and *Z* isomers of the alkene substituent. However, although there are two sets of signals corresponding to each isomer in the ^{1}H NMR spectrum, the coupling between them is complex and it is not possible to assign the spectrum to each isomer.

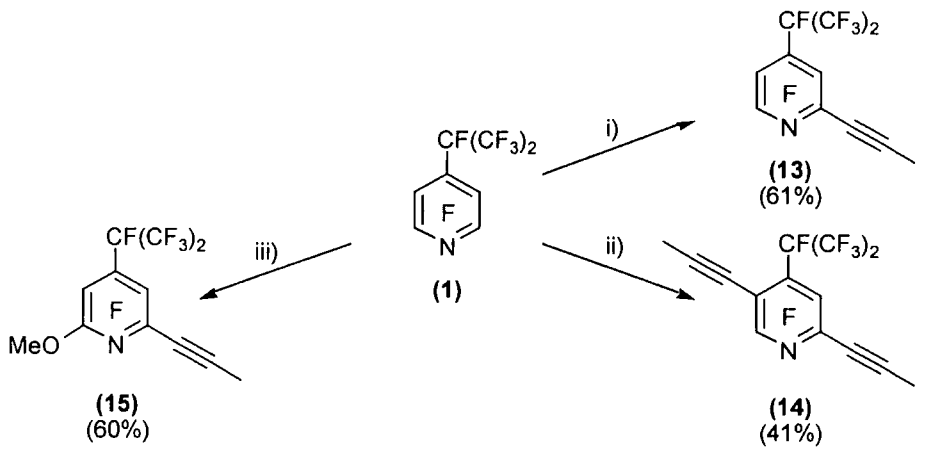
Reaction of **(1)** with phenylmagnesium chloride afforded compound **(11)** in low yield and was accompanied by significant amounts of biphenyl as a side product. The biphenyl is most likely a result of a single electron transfer process, and has been previously reported.[55]



Attempts to introduce a second phenyl group using excess phenylmagnesium chloride were unsuccessful, biphenyl being the major product. Therefore, a different Grignard reagent was selected, and the reaction of phenylmagnesium bromide with **(1)** gives the di-substituted compound **(12)** in fair yield with biphenyl being a minor component. It is not certain why phenylmagnesium bromide should be a more effective reagent for nucleophilic aromatic substitution of a phenyl group than is phenylmagnesium chloride.

4.3) sp-Hybridised.

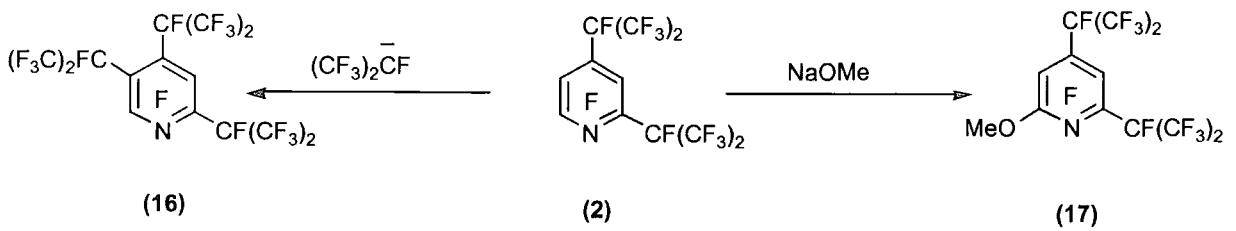
1-Propynylmagnesium bromide was chosen as a suitable model compound for an sp-hybridised carbon-centred nucleophile and a reaction of **(1)** an equivalent of propynylmagnesium bromide afforded the mono- substituted derivative **(13)**, scheme 3. The introduction of a second propynyl group was achieved by reacting **(1)** with an excess of 1-propynylmagnesium bromide affording compound **(14)**. However, surprisingly, substitution of the second propynyl group occurred at the 3-position, *para-* to the first propynyl group at the 6-position, giving the unsymmetrical product **(14)**. This was confirmed by ^{19}F NMR spectroscopy, which showed two resonances for the ring fluorine atoms at –62.3 ppm attributed to the 2-fluorine and at –117.8 ppm assigned for the 5-fluorine atom. If substitution had occurred at the 2- and 6-positions in a manner similar to that observed in the sp^3 and sp^2 series of carbon-centred nucleophiles, the product would have been symmetrical and only one signal for the 3,5-fluorines would have been observed, and that is not the case here. In contrast, a reaction of **(13)** with sodium methoxide in methanol gave compound **(15)**, which clearly shows substitution by methoxide at the 2-position, thereby giving a 2,6-disubstituted product.



Reagents and Conditions
i) 1-propenylmagnesium bromide 1eq. / THF / 65 °C / 20 h. ii) 1-propenylmagnesium bromide 2.5 eq.
iii) 1-propenylmagnesium bromide 1eq. / THF / 65 °C / 20 h. then NaOMe 1 eq. / MeOH / 65 °C / 3h.

(Scheme 3)

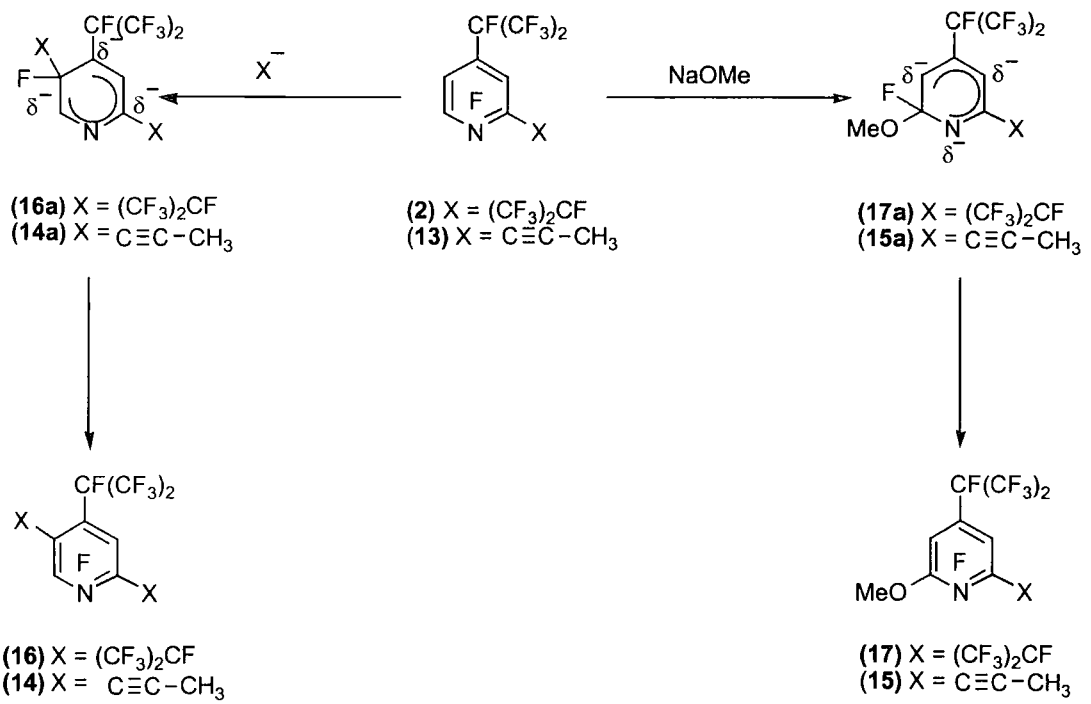
A similar substitution pattern is observed in the reactions of compound **(2)** with the carbon-centred nucleophile $(CF_3)_2CF$ and results in substitution at the kinetically favourable 3-position to give a 3,4,6-tri-substituted product **(16)**, whereas reaction of **(2)** with the oxygen-centred nucleophile methoxide results in substitution at the 2-position giving **(17)**, scheme 4.



(16) **(2)** **(17)**

(Scheme 4)

The formation of **(16)** is the result of the highly activating influence of the two perfluoroalkyl groups and a transition-state for the reaction resembles **(16a)**. Similarly, a propynyl group must also be strongly activating and carbanion stabilising and the transition-state leading to **(14)** resembles **(14a).**



(16a) X = $(CF_3)_2CF$
(14a) X = $C{\equiv}C-CH_3$

(2) X = $(CF_3)_2CF$
(13) X = $C{\equiv}C-CH_3$

(17a) X = $(CF_3)_2CF$
(15a) X = $C{\equiv}C-CH_3$

(16) X = $(CF_3)_2CF$
(14) X = $C{\equiv}C-CH_3$

(17) X = $(CF_3)_2CF$
(15) X = $C{\equiv}C-CH_3$

(Scheme 5)

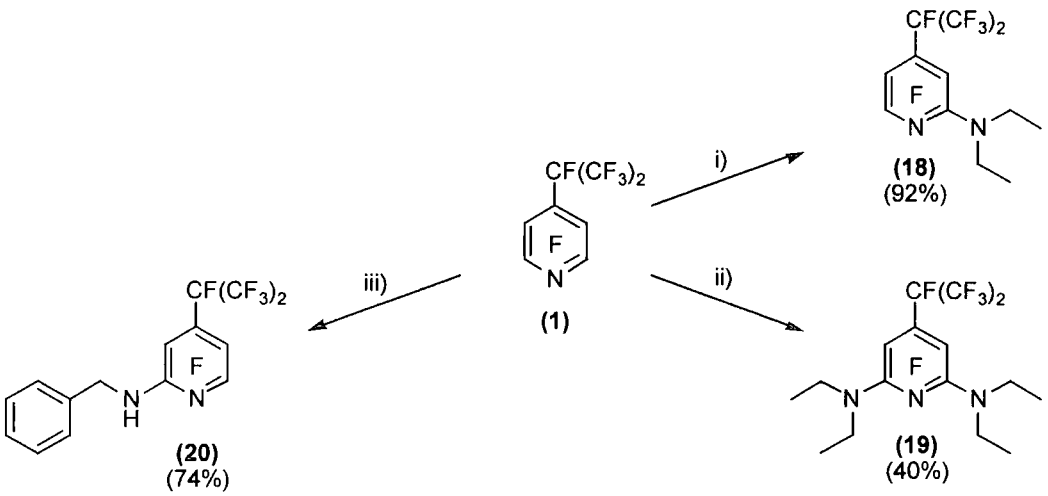
However, we have to consider the observed substitution pattern by methoxide in compounds **(2)** and **(13)**, and there are two possible explanations: a) the reaction with methoxide is reversible, however this has not been observed experimentally; b) methoxide is a much harder nucleophile than the carbon-centred nucleophiles propynyl and $(CF_3)_2CF$ and, therefore, initial-state inductive effects are dominant in the transition-state.

Therefore, it is likely that attack by methoxide produces an early transition-state (**15a** and **17a**) in which attack is favoured at the most electron-deficient site, in this case the carbon *ortho-* to the ring nitrogen atom. In the case of attack by softer, carbon-centred nucleophiles, a later transition-state is produced in which charge-stabilisation is dominant and the effect of carbanion stabilising substituents is more important. The situation is summarised in scheme 5.

The reactions of **(1)** with sp-hybridised carbon-centred nucleophiles give different orientations of substitution than was observed for sp^3 and sp^2-hybridised nucleophiles. Whereas substitution in **(1)** by sp^3 and sp^2-hybridsied nucleophiles gave exclusively 2,6-substituted derivatives, the position of further substitution in mono-substituted derivatives of **(1)** in the sp-hydridised series was found to be dependant on the attacking nucleophile.

5) Reactions of (1) with Nitrogen-Centred Nucleophiles.

The reactivity of **(1)** toward nitrogen-centred nucleophiles was assessed using diethylamine and benzylamine and both reagents were found to be sufficiently nucleophilic to react with **(1)** directly to give the mono- and di-substituted compounds shown in scheme 6.



Reagents and Conditions
i) Diethylamine / THF / 65 °C / 20 h. ii) Diethylamine / THF / 65 °C / 4 d.
iii) Benzylamine / THF / 65 °C / 30 min.

(Scheme 6)

In each case, an excess of the nucleophile was required.

Substitution is preferred at the 2- and 6-positions and this was confirmed by ^{19}F NMR spectroscopy following the arguments described earlier.

The introduction of two nitrogen-centred nucleophiles into **(1)** was found to be considerably more difficult than for the introduction of two oxygen or carbon-centred nucleophiles and an excess of reagent and prolonged heating were required to afford reasonable quantities of **(19)**. This evidence suggests that a nitrogen substituent is more deactivating to further nucleophilic attack in **(1)** than either than a carbon or oxygen substituent at the same position.

6) Conclusions.

In this chapter we have conducted a systematic study of the chemistry of **(1)** with a range of nucleophiles. In general **(1)** was found to readily undergo nucleophilic aromatic substitution with a variety of different nucleophiles to give mono-, di-, and in two cases, tri-substituted derivatives. The orientation of attack by nucleophiles was at the 2- and 6-positions, with the exception of derivatives bearing a propynyl group, which was found to direct substitution at the 3,5-positions in some cases.

The perfluoroisopropyl group in **(1)** and its derivatives undergoes rapid rotation at room temperature, giving rise to two different conformational isomers. The activation energy for the barrier to rotation of the perfluoroisopropyl group in some derivatives of **(1)** was determined.

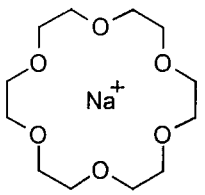
Chapter III Highly Fluorinated Macrocyclic Compounds from S_NAr Reactions.

1) Macrocyclic Chemistry.

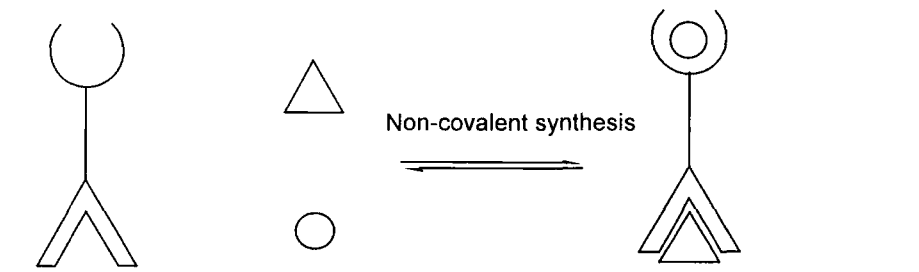
1.1) General Introduction.

In 1960 Pederson discovered the crown-ethers and observed, from a space-filling model that a sodium ion can sit in the cavity of the crown-ether.[56] It is held in position by attractive electrostatic ion-dipole interactions between the alkali metal cation and the six donor atoms of the polyether ring.

He recognised that the increased solubility of the macrocycle in hydroxylic solvents in the presence of sodium ions was due to the crown-ether binding with sodium ions and forming a supramolecular complex.



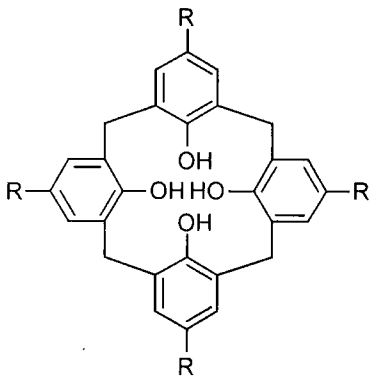
This was early work in what has now become a major area of chemistry, known as molecular recognition involving the study of poly-molecular entities and assemblies. That is, supramolecular complexes formed between two or more designed chemical species which are held together by non-covalent forces.



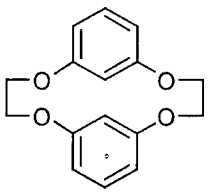
The most elegant examples of complementary molecular systems are biological in origin. For example, an enzyme may catalyse a single reaction with total specificity, because the active site of the enzyme is complementary with the substrate. There are numerous

examples of macrocyclic compounds that form supramolecular complexes in nature. Valinomycin, a naturally occurring macrocyclic antibiotic, is able to selectively transport potassium cations through mitochondrial membranes by formation of a supramolecular complex with a potassium cation.[57]

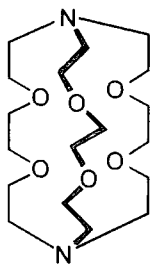
Chemists have produced an enormous range of synthetic macrocyclic molecules with a wide range of co-ordinating and complexation properties, such as, crown-ethers, calixarenes, cyclophanes (macrocycles containing aromatic subunits as part of the ring) and cryptands (cage-like structures).[57] The structural features of macrocyclic compounds can be designed by the chemist in ways that impart specific binding and complexation properties into a system.



A Calixarene

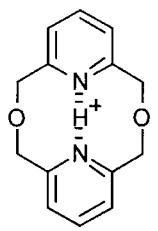


A Cyclophane



A Cryptand

The incorporation of heterocyclic units on the periphery of macrocyclic compounds can impart unique chemical, physical and biological properties into the macrocyclic system. Heterocyclic subunits can participate in complexation through donor atoms; for example, macrocycle **(21)** can co-ordinate a proton through its nitrogen lone-pair orbitals.[58] Also increased stability and rigidity have been observed.



(21)

The work presented in this chapter involves the synthesis of highly fluorinated macrocyclic compounds containing 2,6-substituted pyridine subunits, bridged with oxygen and/or nitrogen containing 'backbones'. These highly fluorinated macrocycles are made through a series of S_NAr reactions in which fluoride is displaced. Before this work

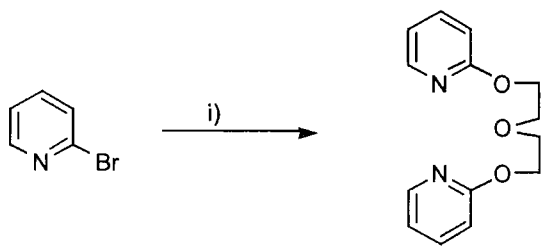
is described, it is appropriate to outline some other macrocyclic compounds that have been made via similar S_NAr type processes.

We begin by examining the synthesis of 2,6-distubstituted pyridine-bridged macrocycles via S_NAr reactions before moving on to describe some other systems, looking at bromide, chloride and finally fluoride as leaving groups. This text is not a comprehensive review but is intended to introduce the reader to the area and give appropriate background and perspective to our study.

1.2) Macrocyclic Compounds via S_NAr Reactions.

Newkome and co-workers have reported the nucleophilic displacement of bromide by oxygen-centred nucleophiles via an S_NAr mechanism to give a variety of 2,6-pyridine-bridged macrocyclic compounds.[59, 60]

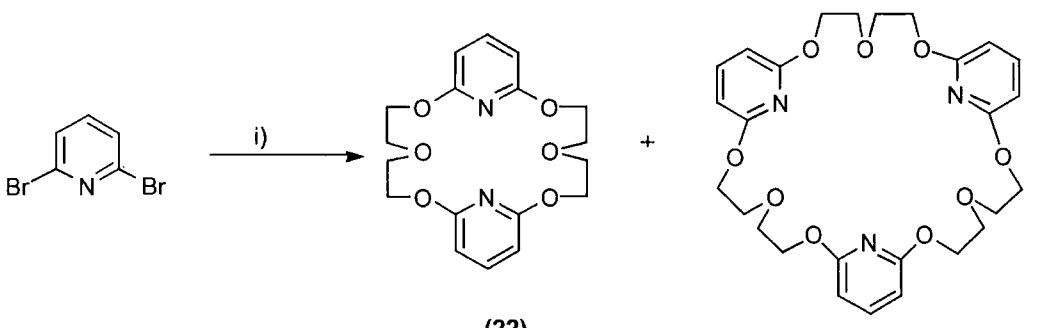
In order to ascertain the generality of these reactions, 2-bromopyridine was treated with diethylene glycol dianion affording the expected ethereal product **(22a)**.



(22a)
(35%)

Reagents
i) NaH / $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$

Therefore, using a difunctional electrophile such as 2,6-dibromopyridine with diethylene glycol dianion, the heteroaromatic ethers **(22)** and **(23)** were produced via intermediates similar to **(22a)**.



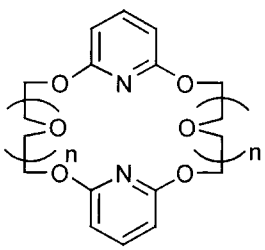
(22)
(7%)

(23)
(2%)

Reagents
i) NaH / $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$

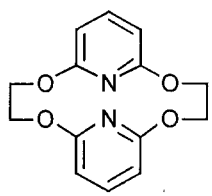
Whereas previous methodology for the synthesis of oxygen-bridged macrocycles produced compounds in which the oxygen atoms are isolated from the pyridine nucleus by methylene groups[58], this reaction demonstrated that direct attachment of oxygen to the ring was possible.

Expanding on this work, Newkome has produced both larger and smaller ring systems using a series of S_NAr reactions with 2,6-dibromopyridine and oxygen-centred nucleophiles. Larger macrocyclic rings were obtained using a range of polyether alcohols to give macrocycles **(24)**, whereas a smaller macrocyclic compound was obtained using ethylene glycol and sodium hydride.



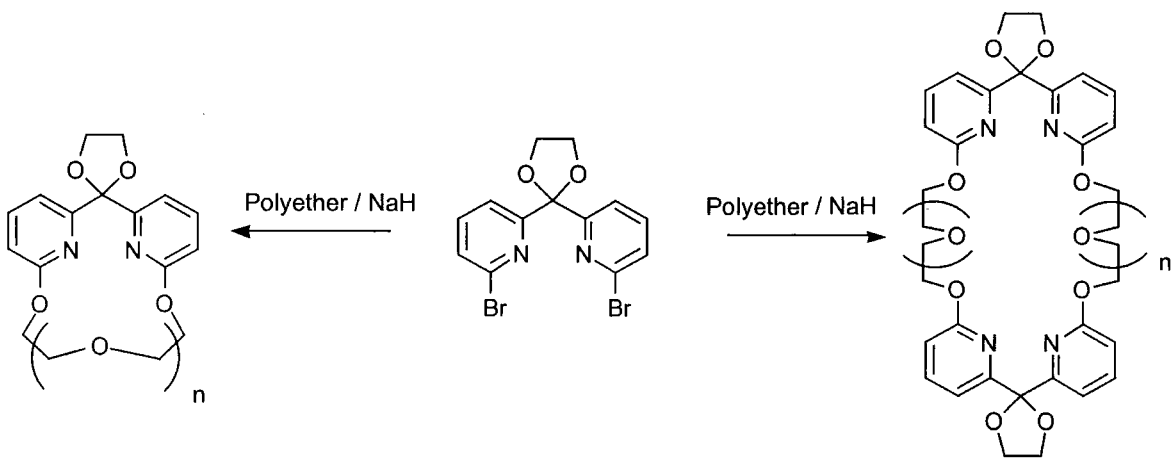
n = 2, 3, 4, 5

(24)
(2% - 48%)



(25)
(16%)

The nucleophilic displacement of bromide from pyridine units has also been investigated in the synthesis of macrocyclic compounds based on bis(2-pyridyl) ketone compounds.[61] In this work two distinct types of macrocycle were made via S_NAr reactions: a) those containing one heterocyclic subunit (1:1 macrocycles), **(26)** and b) those containing two heterocyclic subunits (2:2 macrocycles), **(27)**.



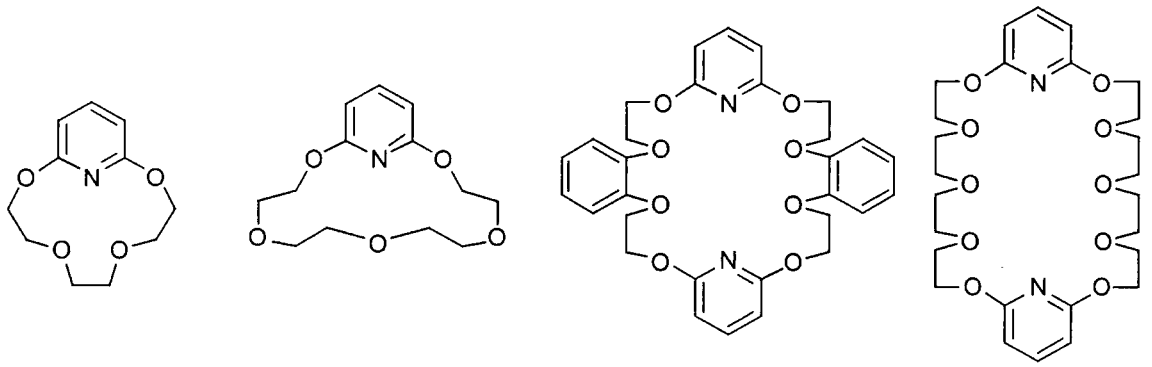
(26)

n = 0, 1, 2, 3, 4, 5

(27)

The introduction of a bipyridyl unit into the polyether chain of a macrocycle was found to dominate the conformations of such compounds, which resulted in the synthesis of a series macrocyclic materials with unusually rigid geometry. This work demonstrates the large conformational and structural effects heteroaromatic units can impart into a macrocyclic system.

Singh and co-workers have produced a series of macrocyclic compound via the S_NAr displacement of chloride from 2,6-dichloropyridine, for example, 2,6-dichloropyridine was reacted with both triethylene glycol and tetraethylene glycol which afforded the 1:1 type macrocycles **(28)** and **(29)**.[62] Introduction of two pyridine units to give 2:2 type macrocycles **(30)** and **(31)**, in a similar fashion to previous work by Newkome, was achieved using the appropriate stoichometry.



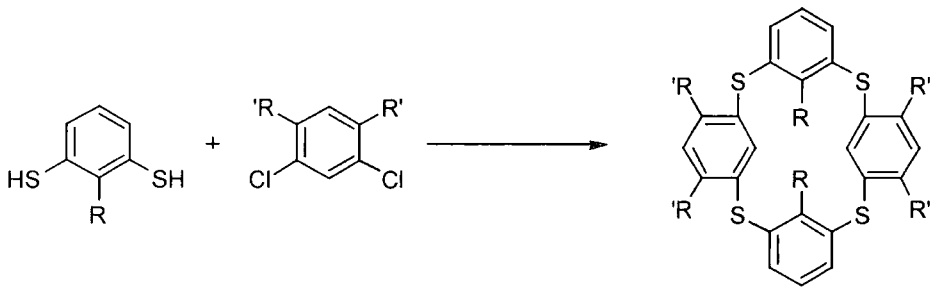
(28) **(29)** **(30)** **(31)**

The complexation and binding properties of these macrocycles were subsequently studied using a series of metal picrate extraction techniques. The ability to bind various metal cations in solution varied greatly with the macrocycle in question, for example, macrocycle **(28)** was found to bind poorly with metals such as Li, Na, K, Tl, whereas, macrocycle **(29)**, which differs from **(28)** by one CH_2CH_2O unit, was shown to bind with Tl effectively and selectively. Although the workers carried out extensive metal extraction and ion-transport studies on these macrocycles, there is no real explanation of how the structure of the system effects its co-ordinating and binding ability.

Techniques used in establishing ligand co-ordination by a macrocyclic species include: metal ion extraction, ion-transport studies, UV spectroscopy, NMR spectroscopy, and electrospray mass spectrometry.[63]

S_NAr displacement of chloride has been utilised in non-heteroaromatic systems by Mullen in the synthesis of tetrathia[1.1.1]metacyclophane compounds. In this case a

sulfur substituent is used in the nucleophilic replacement of chlorine producing a macrocycle which is linked together via phenyl subunits **(32)**.[64]



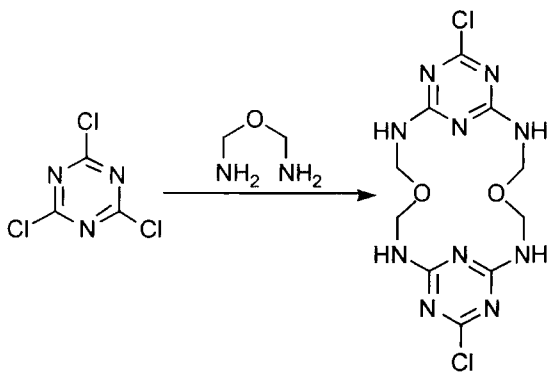
R = H, ^{t}Bu, C_6H_{13}

R' = COPh

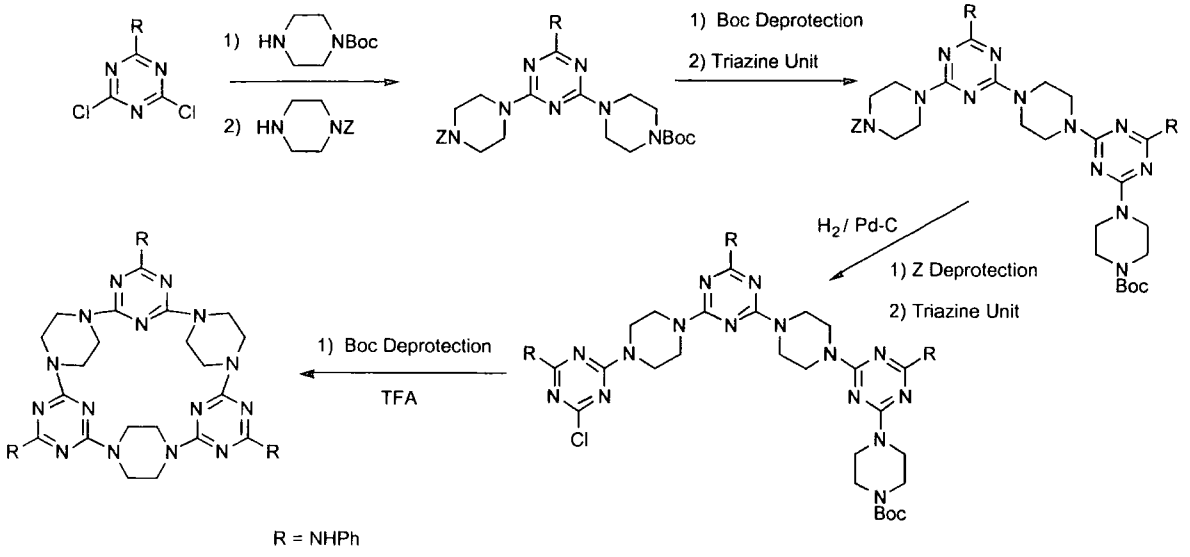
(32)

This work demonstrates that S_NAr type reactions can be used to create macrocyclic compounds from a variety of difunctional subunits.

In addition to pyridine and phenyl subunits, chlorinated triazine compounds have been used in the synthesis of macrocyclic compounds via S_NAr reactions. For example, Montanari and co-workers have produced a series of over 30 macrocycles based on the S_NAr replacement of chlorine in trichloro-s-triazine, such as, the reaction of trichlorotriazine with a diamine to give the macrocycle shown below.[65]



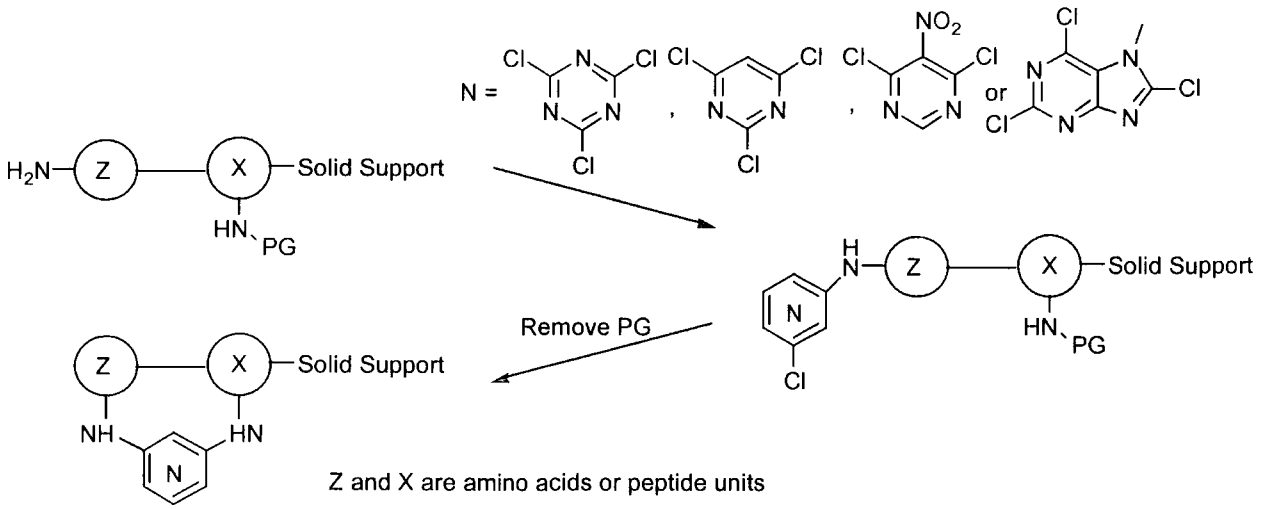
Triazine units have also been utilised by Lowe in the stepwise synthesis of triazine-based macrocyclic scaffolds. The synthesis involves a series of nucleophilic aromatic substitution reactions between partially protected piperazine units and a chlorinated triazine derivative.[66]



At each stage of the synthesis, the chain can be either elongated or cyclised to the macrocycle of interest, and the use of two orthogonal protecting groups on either side of the oligomers allows control of the triazine-piperazine chain. So far a variety of cyclic trimers have been successfully synthesised.

Recently, a series of sequential S_NAr reactions of partially protected amino groups of peptides with chlorinated heterocyclic compounds have been used in the synthesis of macrocyclic peptidomimetic materials.[67] These reactions could lead to especially useful compounds because the cyclization of a peptide structure using rigid groups is well suited for stabilising a bioactive conformation.

The synthesis is performed via a two-step procedure involving incorporation of the aromatic system into the linear peptide chain and subsequent cyclization utilising another S_NAr reaction. Several chlorinated heteroaromatic compounds have been used as subunits and the general procedure of the reaction is outlined in scheme 7.

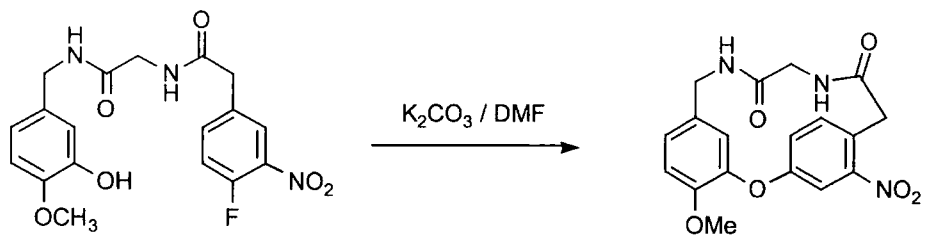


General cyclization procedure for linear oligomers Z-X bearing two orthogonally protected amino groups by S_NAr reactions at chlorinated heteroaromatic systems

(Scheme 7)

Similar cyclisation reactions involving peptide chains have been employed in the synthesis of glycopeptides and vancomycin derivatives using the nucleophilic aromatic substitution of fluoride from 2-fluoro-nitrobenzene derivatives in the ring-forming step.

Roussi and co-workers have reported the intramolecular S_NAr reaction of a linear peptide precursor with a terminal *ortho-* fluoro-nitro group giving the 15-membered macrocycle **(33)**, which is a model for Kistamycin, an antibiotic compound.[68]



(33)

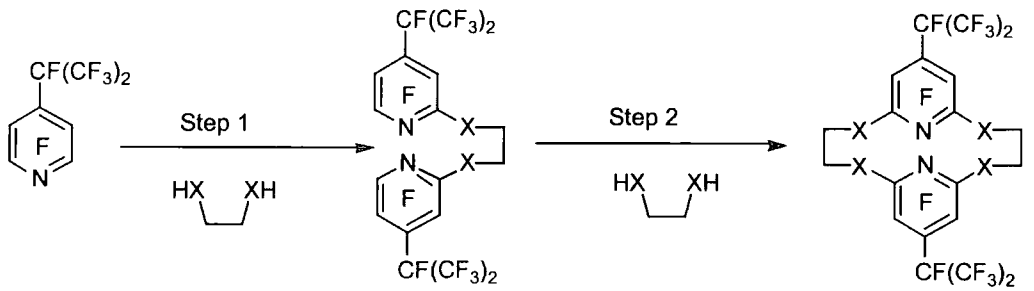
2) Synthesis of Highly Fluorinated Macrocyclic Compounds.

In our own work, we aim to synthesise a range of highly fluorinated macrocyclic compounds from perfluoro-4-isopropylpyridine **(1)**. Earlier work in these laboratories has demonstrated that perfluoro-4-isopropylpyridine units can be joined together using a difunctional nucleophile, such as ethylene glycol dianion, to produce a bispyridyl species which could subsequently be cyclised with another difunctional nucleophile[51], section 2.1. We aim to expand on this early work and develop efficient methodology for the synthesis of a range of macrocyclic compounds derived from **(1)**. An investigation of the complexation ability and structural features of some of these compounds will also be described.

2.1) Macrocyclic Compounds from Perfluoro-4-isopropylpyridine.

2.1.1) Symmetrical Macrocycles.

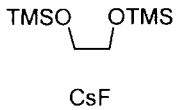
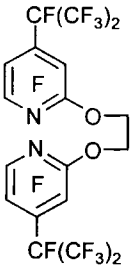
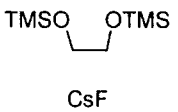
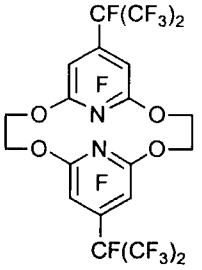
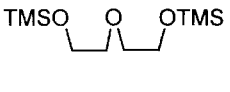
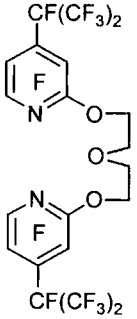
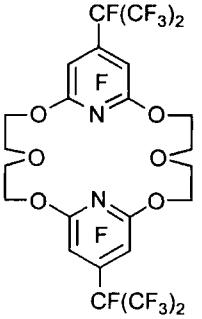
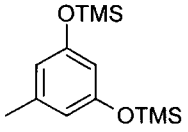
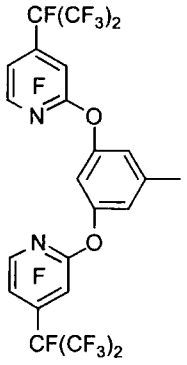
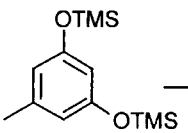
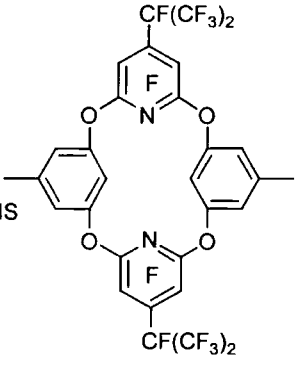
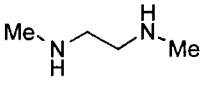
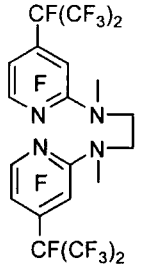
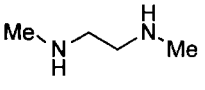
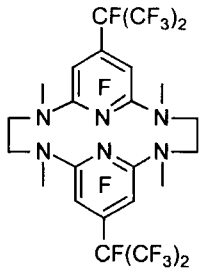
Perfluoro-4-isopropylpyridine **(1)** reacts with a variety of oxygen-centred nucleophiles and a nitrogen-centred nucleophile to produce a series of bispyridyl intermediates, which were subsequently cyclised to the corresponding macrocyclic compounds in the manner illustrated in scheme 8. ^{19}F NMR spectroscopy confirmed that substitution in this series had occurred at the 2- and 6-positions using the same arguments set out in chapter II. Using this methodology, a series of symmetrically substituted macrocyclic compounds have been synthesised, table 2.



X = NMe, O

(Scheme 8)

Table 2.

Reagents for Step 1	Bispyridyl Intermediate	Reagents for Step 2	Macrocycle
 CsF	 **(34)** (94%)	 CsF	 **(35)** (43%)
 CsF	 **(36)** (64%)	 CsF	 **(37)** (40%)
 CsF	 **(38)** (90%)	 CsF	 **(39)** (33%)
	 **(40)** (94%)		 **(41)** (14%)

Conditions for step 1: Monoglyme / 85 °C / 1-5 d Conditions for step 2: Monoglyme 85 °C / 5 d

Sequential nucleophilic aromatic substitution reactions by oxygen and nitrogen-centred nucleophiles have produced a series of 14-, 16- and 20-membered macrocyclic compounds, depending on the size of the difunctional nucleophile employed at each step. The nitrogen-centred nucleophiles are sufficiently nucleophilic to react directly with **(1)** and its derivatives; however, the oxygen-centred nucleophiles are activated by producing the dianion. The desilylation of alcohols by fluoride ion has been reported in these laboratories to be a superior method for the activation of alcohols than is deprotonation by sodium metal or sodium hydride and was therefore chosen as the preferred route in this study. Catalytic quantities of CsF are used as a source of fluoride ion which promotes the desilylation of the alcohol functionality and thus activating it as a nucleophile. Nucleophilic substitution of fluorine using this anion proceeds very efficiently, the fluoride ion displaced is then available to promote further desilayation of another TMS group and thus the process is catalytic.

Whereas the oxygen substituted macrocycles **(35)**, **(37)** and **(39)** are obtained in good yields; the yield for the nitrogen substituted macrocycle **(41)** is relatively low. This reflects the deactivating effect of a nitrogen substituent attached to the aromatic ring.

In general, the isolation of the macrocycles is difficult and they require extensive purification by column chromatography and several recrystallisations in order to obtain high purity samples.

2.1.1.1) X-Ray Crystal Structures.

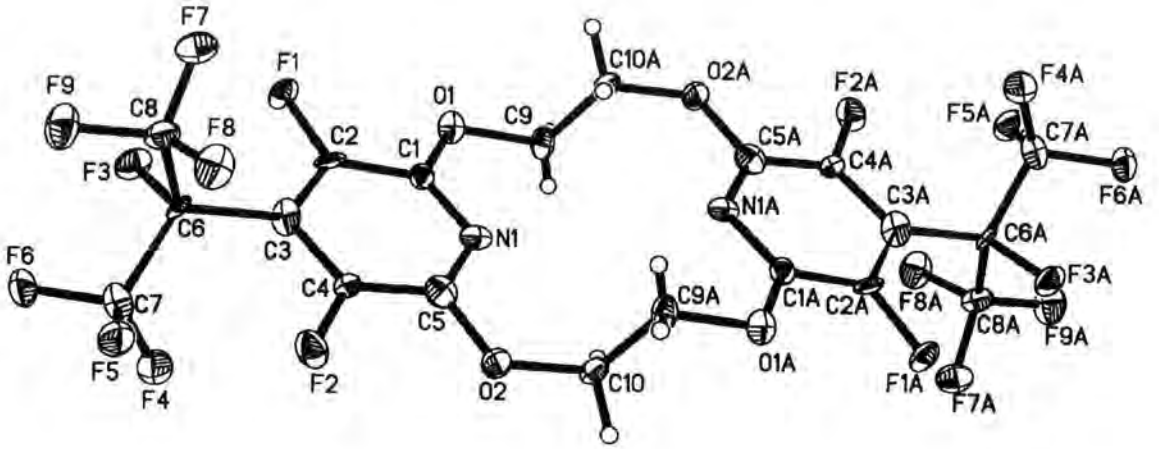
The crystal structures of the oxygen macrocycles **(35)**, **(37)** and **(39)** have been reported[51] (displayed overleaf) and each macrocycle shows a distinctly different structure in the solid state, which will now be described.

Whereas the 14-membered macrocycle **(35)** shows a 'chair-like' structure with the heteroaromatic ring subunits in a planar alignment, the 16- and 20-membered macrocycles **(37)** and **(39)** respectively, both show 'boat-like' structures with π-facing aromatic groups, possibly held in place by π-π aromatic interactions. Macrocycle **(37)** has the two heteroaromatic ring subunits π-facing, in contrast to macrocycle **(39)**, which has the two phenyl groups in a π-facing arrangement. The structure of macrocycle **(39)** is especially unusual; its 'boat-like' structure brings the two relatively bulky perfluoroalkyl groups close together, when perhaps it would be expected for these groups to repel one-another strongly. However, further analysis of the crystal packing of macrocycle **(37)** shows there to be domains of fluorocarbon groups; the macrocycles align themselves so as to place their perfluoroalkyl groups adjacent to those of a neighbouring molecule, however, the reasons for this unusual packing structure are not clear.

The crystal packing of macrocycles **(35)** and **(39)** is difficult to determine due disorder in the perfluoroalkyl groups.

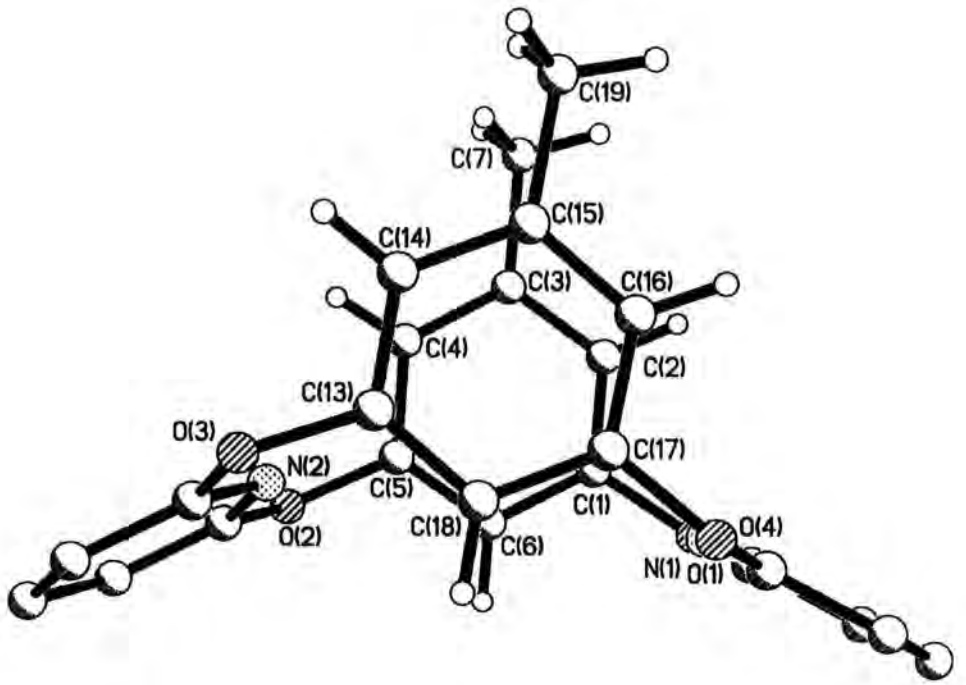
Examination of the interatomic distances in **(37)** shows the adjacent pyridine rings at distance of approximately 4.95 Å apart and based on the cavity size for this 20-membered 'crown-ether-like' macrocycle, a high affinity for potassium ions (cation diameter 2.66 Å) is anticipated. Macrocycle **(39)** shows an interatomic distance between the two facing phenyl groups of approximately 4.53 Å, slightly closer together than the heteroaromatic units in **(37)**. It has a smaller cavity size than **(37)**, but a potassium cation might fit comfortably within this cavity. Macrocycle **(35)** is the smallest of the oxygen series, showing a distance of 3.61 Å between the ring nitrogen atoms, in comparison to 4.95 Å and 4.79 Å in **(37)** and **(39)** respectively. The cavity of **(35)** is a closer model for 15-crown-5 than 18-crown-6, and an affinity for sodium ions (cation radius 1.94 Å) might be predicted.

The x-ray structure of macrocycle **(41)** was not established because suitable crystals could not be obtained.



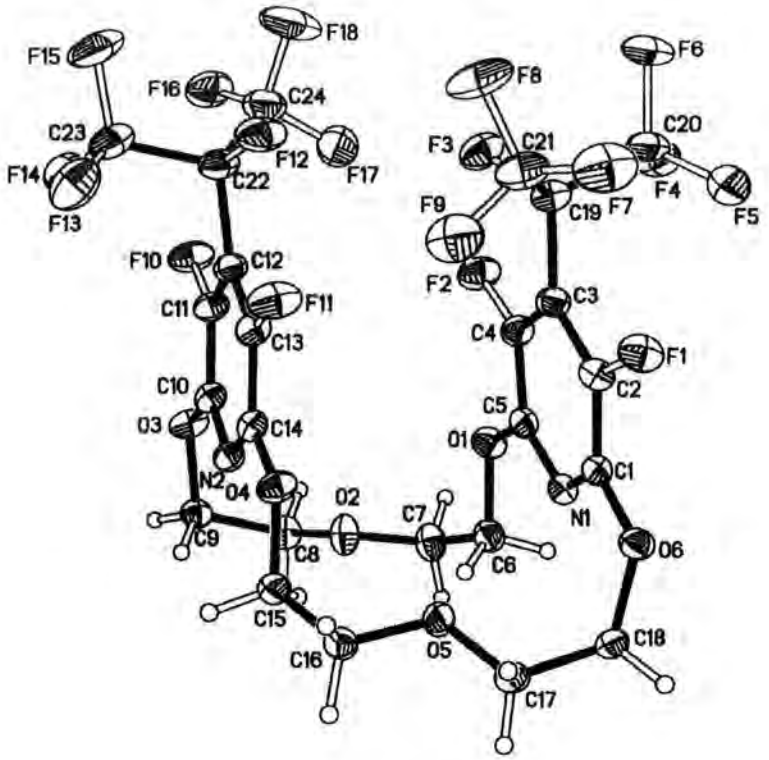
Macrocycle(**35**)

Atoms	Distance (Å)
N1 – N1a	3.61
O1 – O2	4.67
O2 – O2a	6.04



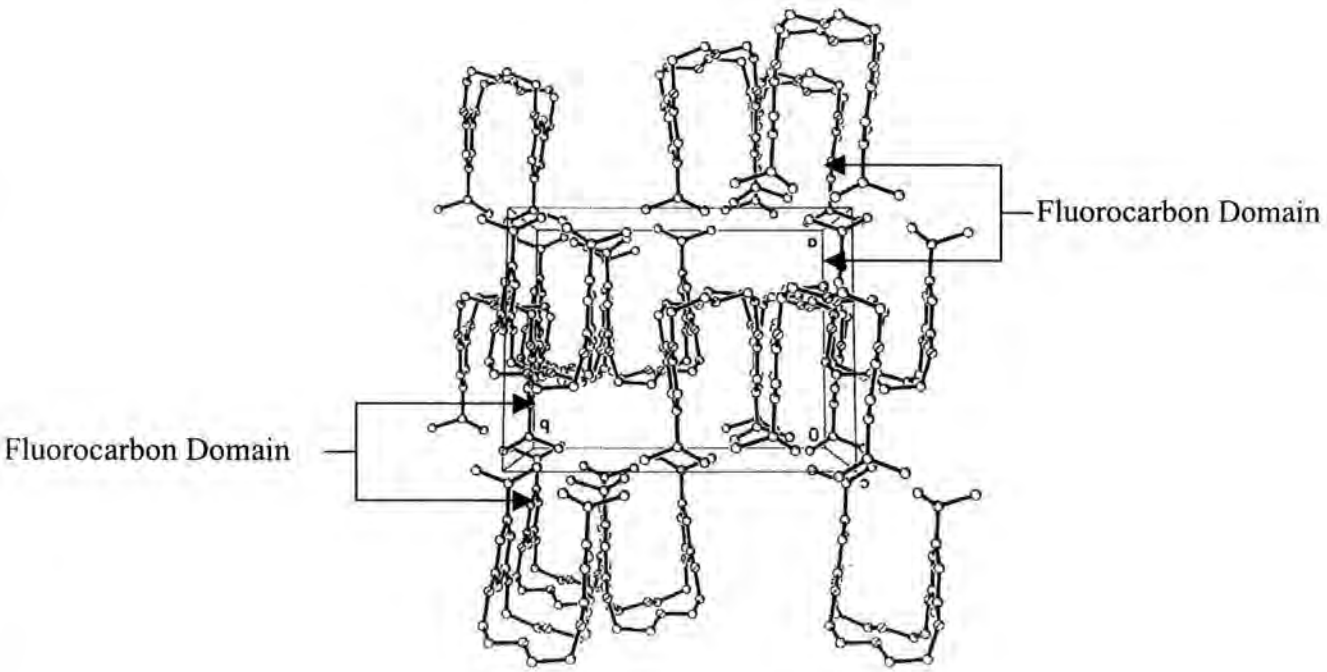
Macrocycle **(41)**; the fluorine atoms are omitted for clarity

Atoms	Distance (Å)
O2 - O4	6.79
O1 - O3	6.55
N1 - N2	4.79
C6 - C18	4.53



Macrocycle **(39)**

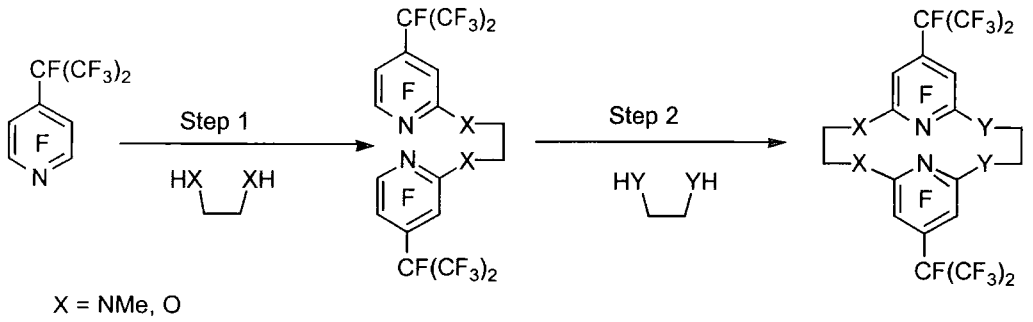
Atoms	Distance (Å)
N1 – N2	4.95
O2 – O5	4.84
N2 – O2	2.91
N1 – O5	2.86



Crystal packing diagram for **(39)**

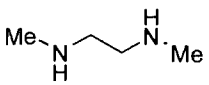
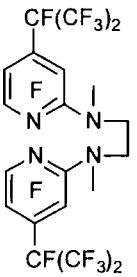
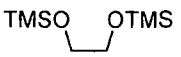
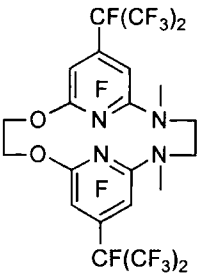
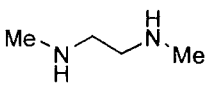
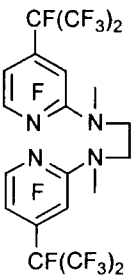
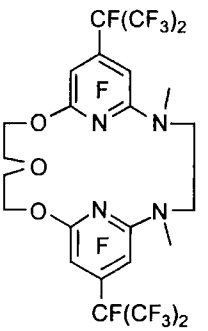
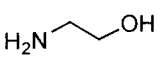
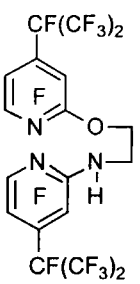
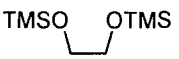
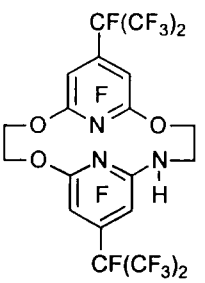
2.1.2) Unsymmetrical Macrocycles.

The step-wise methodology for the synthesis of macrocycles **(35)**, **(37)**, **(39)** and **(41)** employed the same nucleophile in both steps 1 and 2, producing symmetrically substituted compounds. In this series, different nucleophiles for each step have been used to produce a range of macrocycles possessing different 'backbones' linking the heteroaromatic subunits (scheme 8a); we will refer to these as unsymmetrical macrocycles. The results are displayed in table 3.



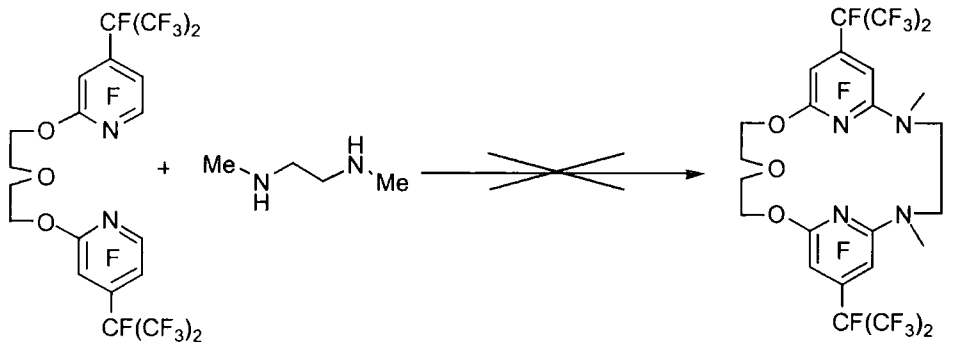
(Scheme 8a)

Table 3.

Reagents for Step 1	Bispyridyl Intermediate	Reagents for Step 2	Macrocycle
	 **(40)** (94%)	 CsF	 **(42)** (20%)
	 **(40)** (94%)	 CsF	 **(43)** (20%)
Step 1  **Step 1a** NaH / **(1)**	 **(44)** (52%)	 CsF	 **(45)** (15%)

Conditions for step 1: THF / 65 °C / 1 Conditions for step 2: Monoglyme 85 °C / 5 d

Macrocycles **(42)** and **(43)** are both derived from the same nitrogen substituted bispyridyl intermediate **(40)** using an oxygen centred-nucleophile in each case to effect cyclisation. Whereas macrocycle **(42)** possess an equal number of bonds between each heteroaromatic subunit, the synthesis of **(43)** employed a larger polyether chain, producing a novel macrocycle with one 'backbone' chain longer than the other. However, in a reverse sequence for the synthesis of **(43)**, a reaction of a diamine with the polyether bispyridyl compound **(36)** did not produce a macrocyclic compound. Newkome and co-workers have also observed similar effects in the synthesis of polyether heteroaromatic macrocycles.[60]

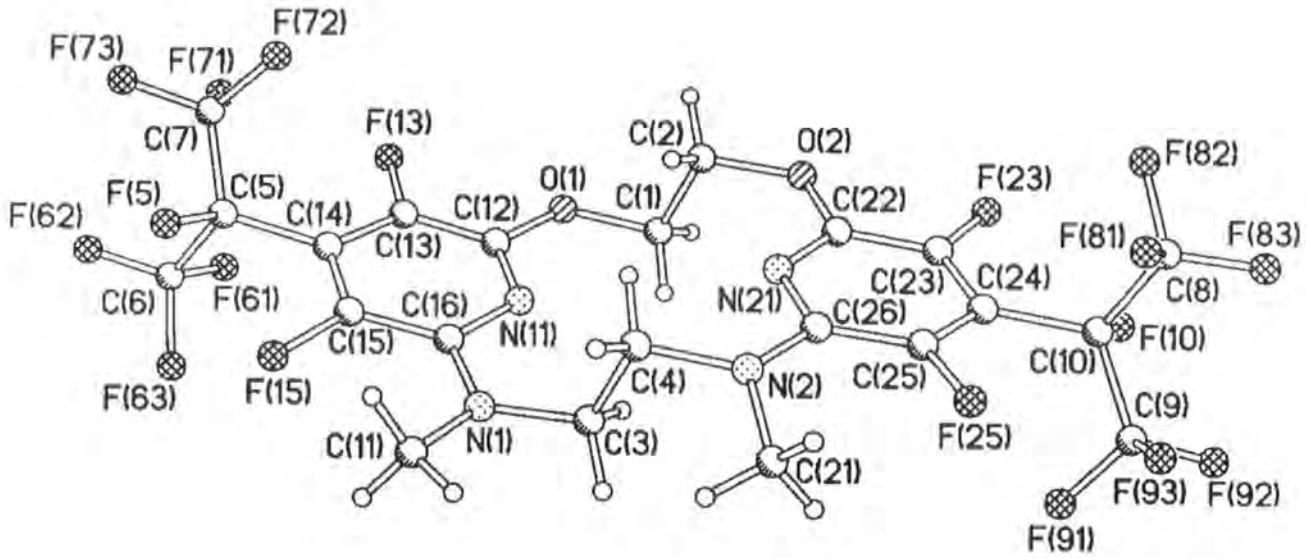


(36) **(43)**

This series of macrocycles demonstrates the versatility of the stepwise methodology and in principle any difunctional nucleophile of suitable size could be used to effect a cyclisation reaction between subunits of **(1)** to give a highly fluorinated macrocyclic compound.

The synthesis of the bispyridyl compound **(44)** is a two step process in which ethanolamine reacts with **(1)** to give a nitrogen substituted derivative, before a reaction of this with sodium hydride in the presence of **(1)** gives the desired intermediate.

The x-ray crystal structure of the 14-membered macrocycle **(42)** was recorded and shows the same 'chair-like' configuration observed for the polyoxygen macrocycle **(35)**.

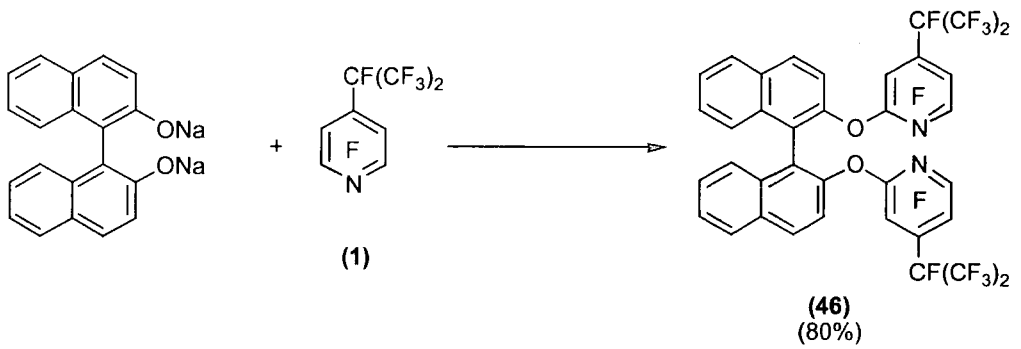


Macrocycle(**42**)

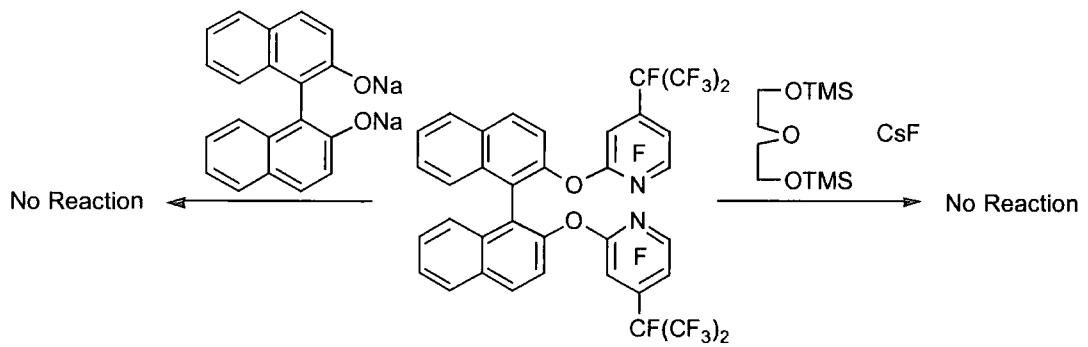
2.2) Reaction of (1) with BINAP

Crown-ethers bearing binapthalene (BINAP) substituents have been used in the stereoselective recognition of chiral substrates[69] and in principle it should be possible to synthesise similar compounds containing highly fluorinated heteroaromatic subunits using the methodology described above.

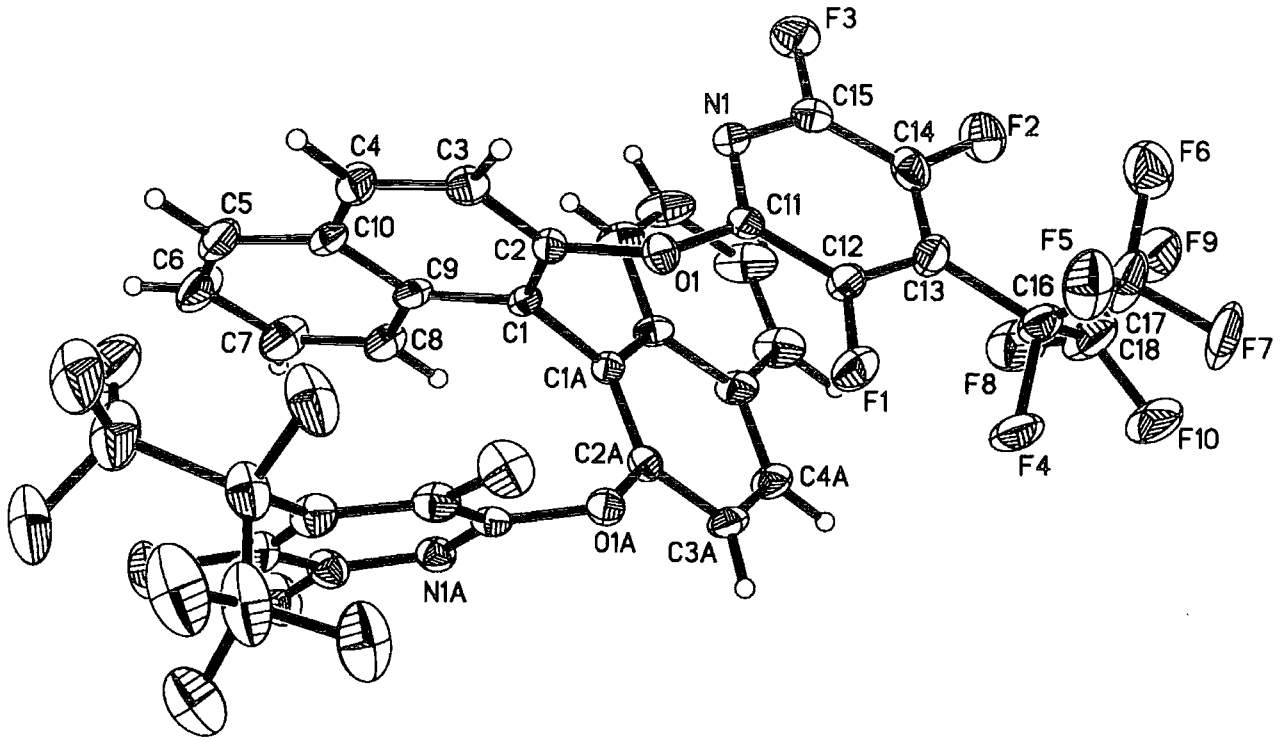
A reaction of **(1)** with the disodium salt of racemic BINAP gave the bispyridyl intermediate **(46)** in excellent yield.



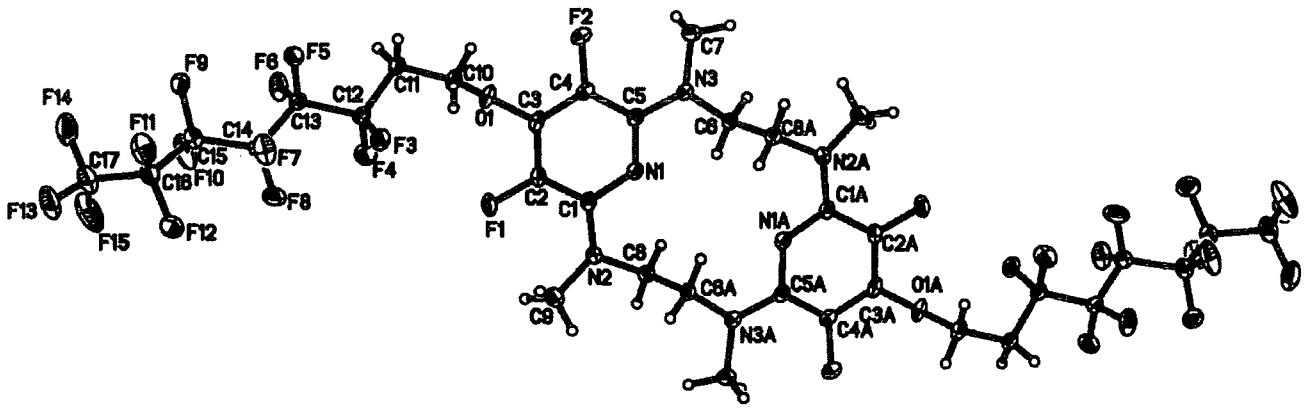
However, cyclisation of **(46)** to a macrocyclic compound could not be achieved using another equivalent of BINAP and was also unsuccessful using diethylene glycol dianion. In both cases no reaction was observed by ^{19}F NMR spectroscopy and the starting materials were recovered. It is not clear why compound **(46)** did not react further with the oxygen-centred nucleophiles displayed.



The x-ray crystal structure of **(46)** has been established and is displayed overleaf.



Compound **(46)**



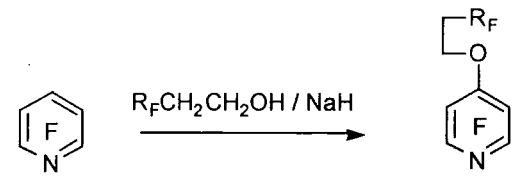
Macrocycle**(49)**

2.3) Macrocycles with Long-Chain Perfluorocarbon Groups.

So far we have discussed the synthesis of macrocyclic compounds derived from **(1)** and in all cases each macrocycle was soluble in perfluorocarbon liquids, such as perfluoromethylcyclohexane (PP2), at elevated temperatures (60 °C), but not at room temperature. It has been suggested that the relative size of a perfluoroalkyl group in a molecule is the key factor in determining its solubility in fluorocarbon media and so, we proposed to introduce a larger perfluoroalkyl group into a pyridine nucleus and synthesise a macrocyclic compound that would be soluble in perfluorocarbon solvents at room temperature.

Fluorous phase chemistry is an expanding area of interest and macrocyclic compounds soluble in perfluorocarbon media might be useful phase-transfer catalysts and be able to transport ligands (e.g. metal ions), which are otherwise insoluble, into such solvents. Also because perfluorocarbon liquids do not form hydrogen bonds and have very low intermolecular forces, studies in such solvents are similar to those carried out in the gas phase.

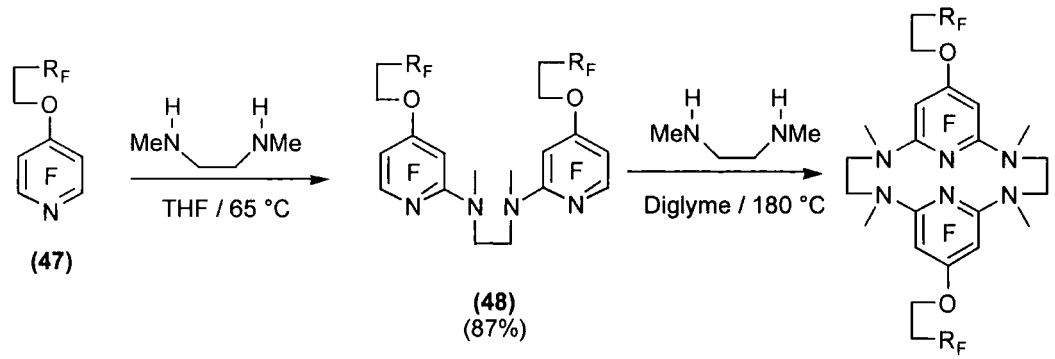
Pentafluoropyridine reacts with a long chain perfluorocarbon alcohol to produce the highly fluorinated heteroaromatic derivative **(47)**.



(47)
(65%)

R_F = $CF_3CF_2CF_2CF_2CF_2CF_2$

Using the step-wise methodology developed above, **(47)** reacts with a diamine to produce the bispyridyl intermediate **(48)** before another reaction with the amine afforded the macrocycle **(49)**.



(47)

(48)
(87%)

(49)
(16%)

R_F = $CF_3CF_2CF_2CF_2CF_2CF_2$

The synthesis of **(48)** proceeds very efficiently and in good yield, in contrast to the second stage where prolonged heating in a higher boiling solvent (180 °C) was required to effect substitution of fluoride in **(48)** and give the macrocycle **(49)**.

Isolation of **(49)** from the diglyme reaction media used was achieved by continuous extraction into a perfluorocarbon liquid (PP2), however, although **(49)** was soluble in such liquids at elevated temperatures (60 °C), it was only sparingly soluble at room temperature.

The x-ray crystal structure of the 14-memebred macrocycle **(49)** shows the same 'chair-like' configuration observed for the other 14-membered macrocycles **(35)** and **(42)**.

3) Characterisation of Macrocycles.

Confirmation that the macrocycles described so far have the 2:2 structure suggested was determined by a combination of ^{19}F NMR spectroscopy and electrospray mass spectrometry.

In each case nucleophilic substitution in the heteroaromatic ring is determined by ^{19}F NMR spectroscopy and the disappearance of a signal at around –90 ppm is consistent with the replacement of a 2- or 6-fluorine atom by a nucleophile (chapter II). If for example, substitution by the nucleophile in step 2 of a macrocyclic synthesis had occurred on only one heteroaromatic unit, to give an acyclic compound, the ^{19}F NMR spectrum would clearly show the remaining 6-fluorine atom at around –90 ppm. This is clearly not the case for the systems described above. However, if cyclisation had occurred to include two bispyridyl subunits to give a 4:4 macrocycle, with twice the mass of those described above, then the ^{19}F NMR spectrum would not discriminate between the two. Therefore, electrospray mass spectrometry was used to establish the correct molecular mass of each macrocycle. For example, a pure sample of macrocycle **(35)** gave an electrospray mass spectrum with a distinct molecular ion peak at 682 *m/z* and this is equal to the molecular mass of the system proposed. Because the electrospray technique is highly sensitive any larger macrocyclic species would be evident in the spectrum, and none are observed. A similar set of experiments was used to verify the structures of all the macrocycles presented here.

However in the synthesis of the macrocycles described an unknown mixture of materials is recovered by column chromatography in addition to the pure 2:2 macrocycle. Analysis of this material was inconclusive, but it is most likely a mixture of acyclic oligmers or larger ring macrocycles that we have been unable to isolate. It is also important to point out that the macrocyclic materials do not irreversibly bind with the

silica gel used in the chromatography purification step, because all of the material is recovered.

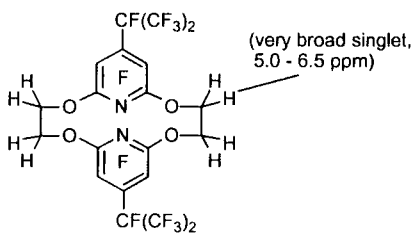
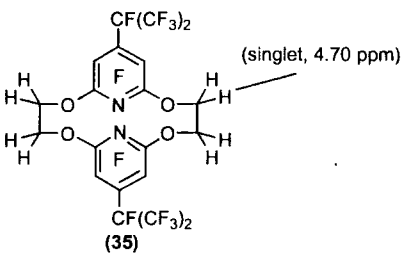
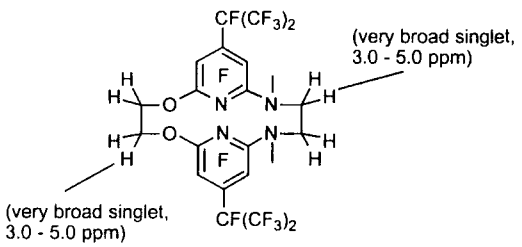
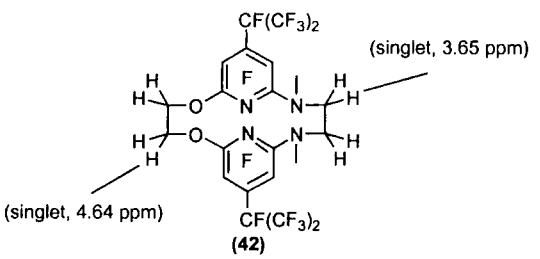
3.1) Conformational Studies.

Variable temperature ^{1}H NMR spectroscopy has been used to examine the macrocycles **(35)**, **(37)**, **(39)** and **(42)**, and possible conformations are considered.

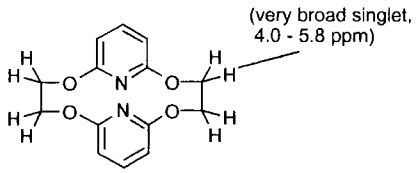
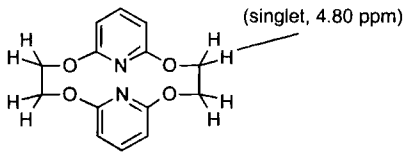
Each of the macrocyclic compounds was dissolved in *d*-tetrachloroethane and its NMR spectrum was recorded at 20 and 90 °C at 400 MHz.

At room temperature the 14-membered macrocycles **(35)** and **(42)** both show very broad signals for the methylene protons of the macrocycle 'backbone'. Macrocycle **(35)** displays a broad resonance between 5.0 and 6.5 ppm for the methylene protons, whereas **(42)** shows a similarly broad signal between 3.0 and 5.0 ppm for both the CH_2O and CH_2N protons. On heating to 90 °C both macrocycles display a sharpening of these methylene signals; **(35)** shows a singlet at 4.70 ppm for the CH_2O protons and **(42)** shows singlets at 3.65 and 4.64 ppm the for the CH_2N and CH_2O protons respectively, table 4.

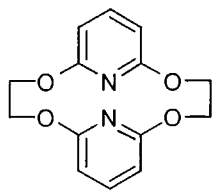
Table 4.

20 °C	90 °C
	
	

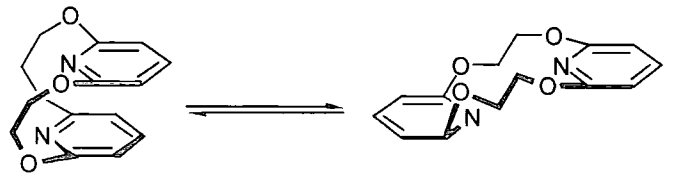
Variable temperature NMR studies have been reported for similar 14-membered macrocyclic systems. Newkome and co-workers have plotted the ^{1}H NMR spectrum of macrocycle **(25)** over a temperature range (shown below) and have observed a similar sharpening of signals at higher temperatures as seen for macrocycles **(35)** and **(42)**.[60]

20 °C	90 °C
 (very broad singlet, 4.0 - 5.8 ppm)	 (singlet, 4.80 ppm)
(25)	

They proposed two possible conformations, which undergo inter-conversion in solution. Therefore, a similar set of conformations might be in operation in **(35)** and **(42)**.

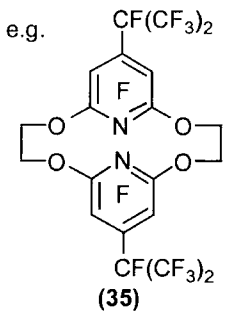


(25)

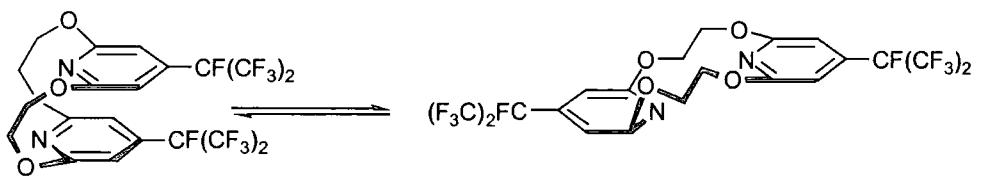


Boat Chair

e.g.



(35)



Boat Chair

For compounds **(35)** and **(42)** at 20 °C the inter-conversion between the two conformations is relatively slow with respect to the NMR time-scale and the result is a very broad signal corresponding to the methylene protons of both conformations. On heating, the rate of inter-conversion becomes relatively 'fast' on the NMR time-scale and a sharpening of the methylene proton signals is observed because the two conformations are indistinguishable. In principle, at lower temperatures, both conformations should appear as separate signals in the ^{1}H NMR spectrum, however, the macrocycles are not sufficiently soluble below room temperature to allow this to be verified.

However, another effect in operation could also account for these observations. Rotation of the perfluoroisopropyl group in **(35)** and **(42)** could result in a broadening of the methylene proton signals in the ^{1}H NMR spectrum and on heating, when rotation of

the perfluoroisopropyl group is more rapid, a sharp signal results. But, if this were the effect in operation, then the same phenomenon would be expected in macrocycle **(37)**, however this has not been observed.

The 16- and 20-memebred macrocycles **(37)** and **(39)** respectively, do not display any significant change in their ^{1}H NMR spectrum over a temperature range of –22 to 90 °C. Therefore, either: a) no conformational changes are occurring in macrocycles **(37)** and **(39)** or b) the conformational changes for **(37)** and **(39)** are very rapid on the NMR time-scale, even at low temperature (-25 °C). And if we consider (a), were the macrocycles **(37)** and **(39)** do not change conformation in solution, it could be envisaged that one type of conformation is stabilised in solution over the other. The x-ray structure of **(37)** and **(39)**, shows a 'boat-like' conformation in which the heteroaromatic rings in **(37)** and the aryl rings in **(39)** are both facing each other, and in principle an aromatic interaction between such groups could stabilise this conformation in solution. In contrast, for macrocycles **(35)** and **(42)**, which both have the 'chair-like' conformation in the x-ray structure, no stabilisation of one conformation is occurring and inter-conversion between the two proposed conformations occurs readily. However, the evidence supporting these arguments is limited and this interpretation is merely speculative.

3.2) Complexation and Binding Studies for (35), (37) and (39).

In principle the oxygen containing macrocycles synthesised so far should posses similar co-ordination properties to other polyether heteroaromatic macrocycles, such as those reported by Newkome. The complexation and binding characteristics of the macrocycles **(35)**, **(37)** and **(39)** have been investigated, and will now be described.

3.2.1) Electrospray Mass Spectrometry.

Electrospray mass spectrometry can be used to probe the ability of metal cations or other species to co-ordinate with suitable ligands such as crown-ethers and other macrocyclic compounds. It is a technique whereby a solution of the macrocycle, is mixed with a solution of a ligand, e.g. alkali metal cations, and this mixture is then injected into the mass spectrometer using an electrospray probe. Binding between the macrocycle and the co-ordinating species is determined by the presence of a *m/z* peak for the mass of the co-ordinating species + macrocycle. The technique is very sensitive and complexation is easily determined by a comparison with a reference sample containing the macrocyclic material only. Two experiments are described which have demonstrated the co-ordinating nature of macrocycles **(35)**, **(37)**, **(39)** in comparison with 18-crown-6 as a reference.

3.2.1.1) Binding with Alkali Metal Cations.

A solution containing sodium acetate (10^{-4} M), potassium acetate (10^{-4} M), and caesium acetate (10^{-4} M) in methanol was carefully prepared. Separate 10^{-4} M solutions of macrocycles **(35)**, **(37)** and **(39)** in methanol were also prepared.

1 ml of the metal acetate mixture and 1 ml of macrocycle **(35)** solution were mixed together in a sample vial before being injected into the mass spectrometer using the electrospray technique. This process was repeated for macrocycles **(37)**, **(39)** and 18-crown-6 as a reference. The results are presented below in table 5, and show the RMM of the macrocycle and the major peaks in the spectrum after mixing with the metal cation solution. *Comment* refers to the species that is likely to be binding with the macrocycle with that *m/z* value. *MS mode* refers to the operation of the mass spectrometer, which can be in one of two configurations, the negative mode and positive mode, which observes negative and positively charged species respectively. Note that in each case below only one of the modes was successful, thus for **(35)** which demonstrates the binding of the acetate counter-ion in the negative mode, no discernible signal was obtained in the positive mode.

Table 5. Macrocycles **(35)**, **(37)** and **(39)** in presence of metal acetates.

Macrocycle	MS Mode	RMM	Major Peaks (*m/z*)	Comment
(35)	-ve	682	717	chloride
			729	acetate
			757	unknown
(37)	+ve	770	793	sodium
			809	potassium
			903	caesium
(39)	-ve	806	941	chloride
			853	acetate
18-crw-6	+ve	264	287	sodium
			303	potassium

Macrocycle **(37)** and 18-crown-6 show co-ordination to all three metal cations in the positive mode, with sodium being the most favourable for **(37)**, and potassium the most favourable for 18-crown-6. Both show no co-ordination with the acetate counter-ion or to any chloride impurities in the negative mode. In contrast, macrocycles **(35)** and **(39)** both exhibit co-ordination to the acetate counter-ion and also to chloride (an impurity) in the

negative mode and show no co-ordination to the metal cations in the positive mode. This was a surprising result as anion binding by macrocyclic compounds is relatively rare and is generally only observed in charged species or compounds with highly acidic hydrogen atoms which co-ordinate to anions via hydrogen bonding. Therefore, we investigated the anion binding ability of this series of macrocycles further using the same technique with a solution of halide anions.

3.2.1.2) Binding with Halide Anions.

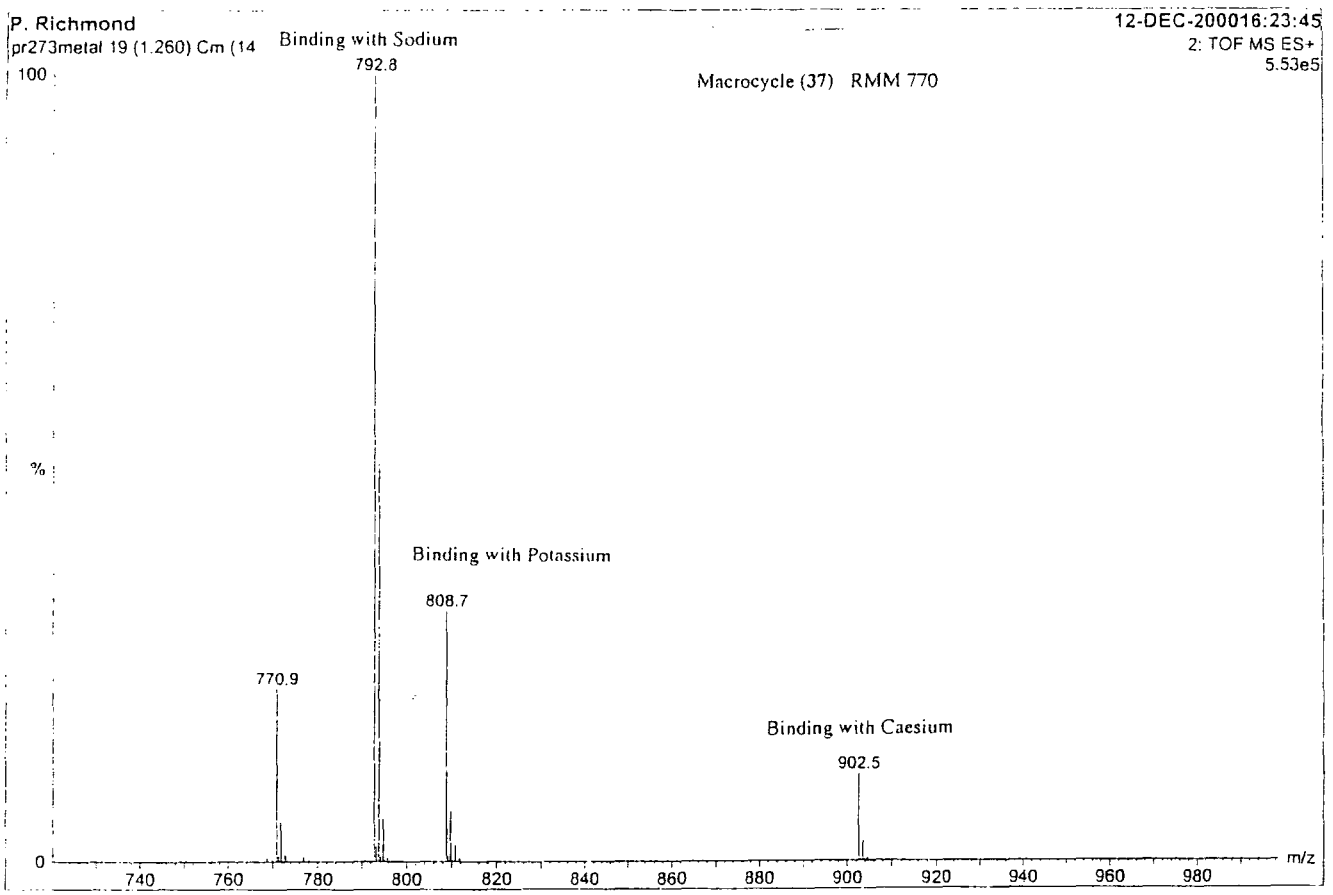
A similar experiment to that above was carried out using a solution of sodium halides instead of metal acetates. 1 ml of macrocycle solution was mixed with 1 ml of a solution containing equimolar amounts of sodium chloride, sodium bromide and sodium iodide in methanol. The electrospray mass spectrometry results for **(35)**, **(37)** and **(39)** are presented below in table 6.

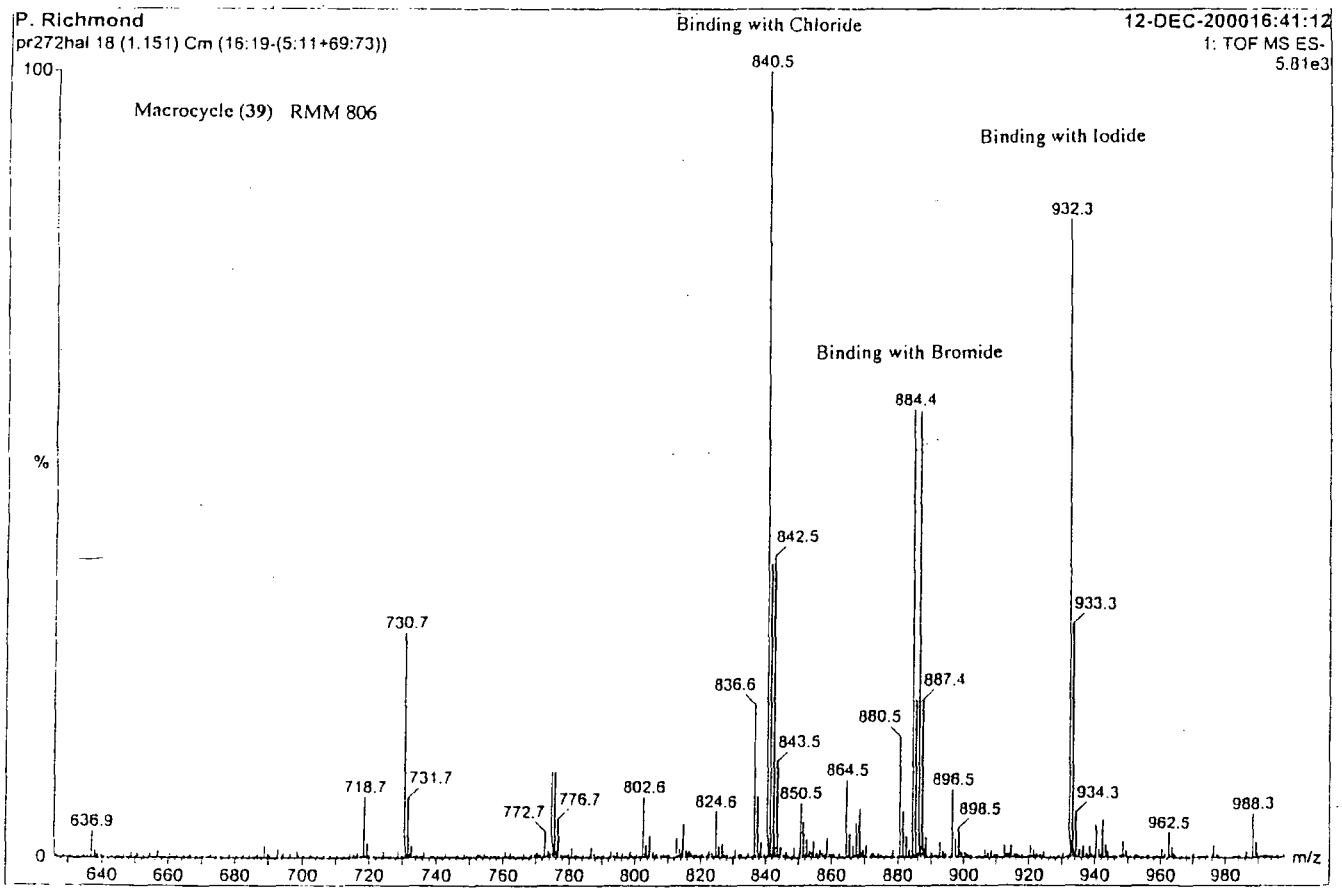
Table 6. Macrocycles **(35)**, **(37)** and **(39)** in presence of sodium halides.

Macrocycle	MS Mode	RMM	Major Peaks (*m/z*)	Comment
(35)	-ve	682	717	chloride
			761	bromide
			809	iodide
(37)	+ve	770	793	sodium
(39)	-ve	806	841	chloride
			884	bromide
			932	iodide
18-crw-6	+ve	264	287	sodium

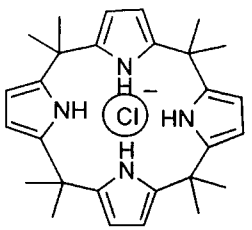
Both macrocycles **(35)** and **(39)** show co-ordination to chloride, bromide and iodide and show no co-ordination to the excess sodium present, whereas macrocycle **(37)** and 18-crown-6 show co-ordination to sodium only.

In summary, both experiments show that, macrocycles **(35)** and **(39)** bind halide and others anions such as acetate, whereas, **(37)** and 18-crown-6 both bind with cations but not anions. The explanation of why **(37)** binds cations can be rationalised by considering the donor ability of the oxygen atoms in the polyether ring in a similar manner to the crown-ethers. However the reasons for anion binding in **(35)** and **(39)** is not clear.

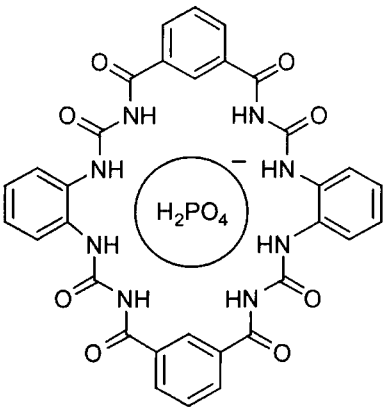

P. Richmond
pr273metal 19 (1.260) Cm (14
12-DEC-200016:23:45
2: TOF MS ES+
5.53e5
Binding with Sodium
792.8
Macrocycle (37) RMM 770
Binding with Potassium
808.7
770.9
Binding with Caesium
902.5
100
%
0
740
760
780
800
820
840
860
880
900
920
940
960
980
m/z


P. Richmond
pr272hal 18 (1.151) Cm (16:19-(5:11+69:73))
Binding with Chloride
12-DEC-200016:41:12
1: TOF MS ES-
5.81e3
100
Macrocycle (39) RMM 806
840.5
Binding with Iodide
932.3
Binding with Bromide
884.4
842.5
933.3
730.7
836.6
887.4
880.5
843.5
864.5
898.5
718.7
731.7
776.7
772.7
802.6
824.6
850.5
934.3
988.3
636.9
962.5
%
0
640
660
680
700
720
740
760
780
800
820
840
860
880
900
920
940
960
980
m/z

As mentioned above, anion binding is comparatively rare to cation binding and as such is less well studied. However, numerous macrocyclic compounds which co-ordinate effectively to anions are known and it is an area of supramolecular chemistry which continues to generate interest.



meso-Octamethylcalix[4]pyrrole



Tetrakisurea macrocycle

Compounds with highly acidic hydrogen atoms can bind anions via hydrogen bonds. For example the pyrrolic protons of a calix[4]pyrrole[57] can bind chloride and the acidic protons in amide linkages have been shown to bind phosphate ions.[70]

Co-ordination to anions has also been observed for charged species, the anion being held in position by electrostatic interactions and also for compounds with dipolar carbonyl bonds, but the binding constants are much weaker than those of hydrogen bonding macrocycles or for charged species. Anion binding is also observed in compounds that can act as Lewis acids, such as organoboron compounds.

However, the macrocycles **(35)** and **(39)** which both show co-ordination to anions in the above experiment do not possess a charge and the protons in such compounds would not expected to be particularly acidic. Therefore, we are unable to explain why macrocycles **(35)** and **(37)** bind with the anions in this series.

3.2.2) ^{1}H NMR Spectroscopy.

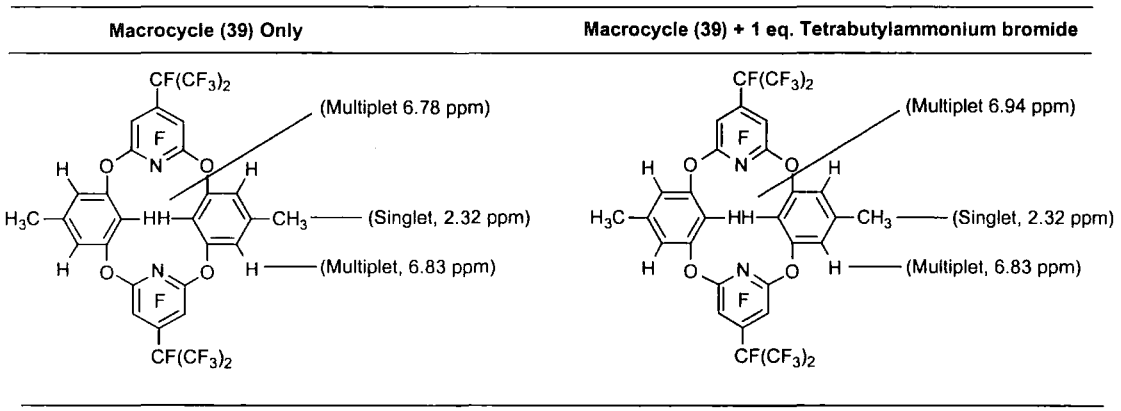
In the above section we have demonstrated that macrocycles **(35)** and **(39)** bind with anions in the gas phase mass spectrometry experiments and we have investigated this phenomenon further.

One of the most powerful methods for the determination of anion binding in solution is by ^{1}H NMR spectroscopy. For example, Reinhoudt and co-workers have examined the anion binding properties of multiple urea binding sites in several macrocyclic and acyclic systems (above) and binding in such compounds is thought to

occur through hydrogen bonding between the acidic protons of the amide linkages and anions such as chloride and phosphate.

The addition of one equivalent of $H_2PO_4^-$ resulted in a large upfield shift over 1 ppm, towards lower frequency, in the ^1H NMR spectrum for the aryl urea and benzylic urea protons and this was attributed to the binding of a phosphate anion.

In our work we have conducted similar experiments with macrocycles **(35)** and **(39)** in the presence of bromide anions. A sample of macrocycle was **(39)** added to an equimolar amount of tetrabutylammonium bromide and the ^1H NMR spectrum was recorded. Examination of the aryl protons shows a significant downfield shift (0.16 ppm), towards higher frequency, for the 2-proton of the aryl units, whilst all the remaining protons remain unchanged.



This is a significant change in the ^1H NMR spectrum and indicates that some degree of binding is occurring, most probably to the tetrabutylammonium cation because the chemical shift change is downfield, in the opposing direction to that observed by Reinhoudt for anion binding. Also a positively charged species near a proton would be expected to be electron withdrawing, deshielding the proton and thus a shift to a higher frequency is observed in the ^1H NMR spectrum.

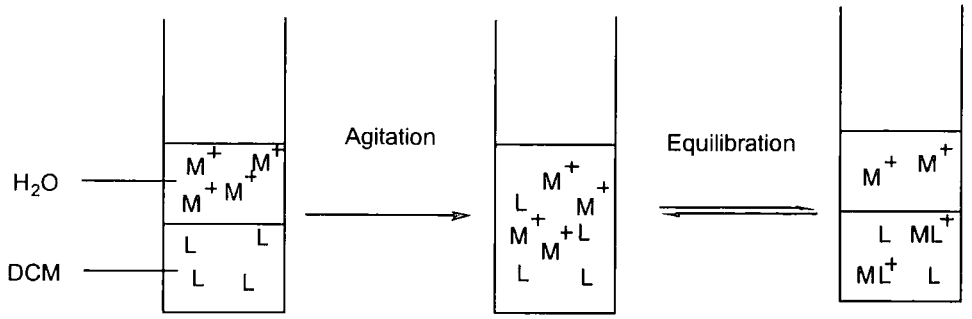
This result demonstrates that, in solution, macrocycle **(39)** binds with the cations and not anions as shown in the above mass spectrometry experiments.

The same experiment was use for compound **(35)** however; the broad peaks for the methylene protons make examination of this macrocycle impossible by this method.

3.2.3) Metal Extraction Studies.

Metal extraction studies have been reported by many workers as a useful method in the determination of the binding ability of macrocyclic compounds with metal cations in

solution. In order to assess the metal-ion transport properties of the macrocycle, aqueous solutions of sodium and potassium picrate were extracted into a dichloromethane solution containing the macrocyclic compound under investigation. The metal picrates are insoluble in the organic layer and can only be taken into the organic solution by the formation of supramolecular complex with the macrocyclic compound.



L = Macrocycle
M^+ = Sodium or potassium picrate
ML^+= Metal-Macrocycle supramolecular complex

The amount of supramolecular complex formed can be determined by UV spectroscopy. A comparison of the absorbance of the metal picrate solution before and after extraction with the organic macrocycle layer gives a value for the percentage of metal picrate extracted.

$$\% \text{ Extraction} = (Abs_{Before} - Abs_{After}) / Abs_{Before} \quad \text{x } 100\%$$

Where Abs_{Before} is the absorbance of the metal picrate layer before agitation and Abs_{After} is the absorbance of the metal picrate aqueous layer after equilibration. The absorbance is measured at a wavelength of 275 nm. The results are displayed in table 7.

Table 7.

	Sodium Picrate			**Potassium Picrate**		
Macrocycle	Abs_{Before}	Abs_{After}	**% Extraction**	Abs_{Before}	Abs_{After}	**% Extraction**
(35)	0.0273	0.0124	**54**	0.0139	0.0832	**40**
(37)	0.0273	0.0250	**9**	0.0139	0.1010	**28**
(39)	0.0273	0.0125	**27**	0.0139	0.0147	**0**
18-Crw-6	0.0273	0.0271	**6**	0.0139	0.0390	**72**

18-Crown-6 shows an excellent affinity and selectively for the extraction of potassium cations which is consistent with the known chemistry of crown-ethers. Macrocycle **(37)** shows good affinity for potassium cations and poor affinity for sodium in contrast to **(39)** that demonstrates good affinity for sodium and poor affinity for potassium. This indicates that the cavity size in macrocycle **(39)** is not large enough to accommodate the larger potassium cation whereas the 20-membered macrocycle **(37)** clearly can. Macrocycle **(35)** shows greater affinity for both sodium and potassium cations than either **(37)** or **(39)**, although none of the macrocycles show an affinity similar to that of 18-crown-6 for potassium.

These results are contradictory to those observed for **(35)** and **(39)** in mass spectrometry experiments, in that they clearly show an affinity for some metal cations in solution whereas this is not observed in the mass spectrometry experiments.

4) Conclusions.

In this chapter we have developed an efficient step-wise methodology for the synthesis of both symmetrical and non-symmetrical macrocyclic compounds using perfluoro-4-isopropypyridine **(1)**. Also, a macrocycle possessing a long-chain fluorocarbon group was synthesised in a similar manner.

Conformations for several of the macrocycles have been proposed and variable temperature ^{1}H NMR spectroscopy studies have enabled us to speculate on the nature of conformational changes in some systems.

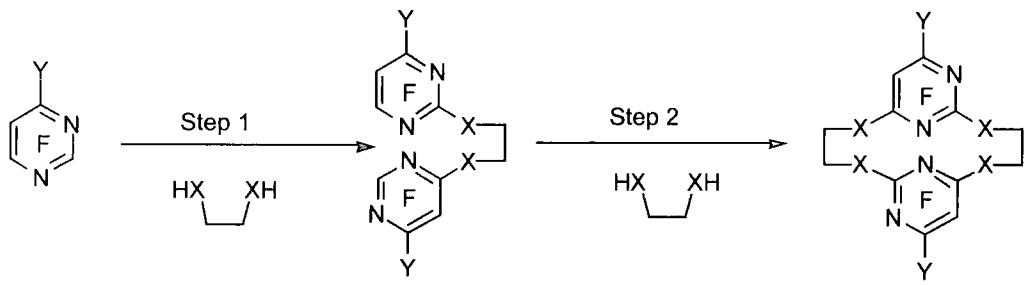
The complexation and binding properties of several macrocycles were investigated by electrospray mass spectrometry and metal ion extraction.

Chapter IV Polyfluoroalklyation and Nucleophilic Aromatic Substitution in Tetrafluoropyrimidine.

1) Introduction.

In the previous chapter we presented the chemistry of a perfluoroalkylated pyridine derivative and its use in the formation of highly fluorinated macrocyclic compounds via nucleophilic aromatic substitution reactions. In this chapter we will explore the chemistry of the tetrafluoropyrimidine system and will examine perfluoroalkylation reactions before looking at nucleophilic aromatic substitution in several tetrafluoropyrimidine derivatives. The aim was to develop a strategy for the synthesis of macrocyclic compounds that contain perfluoroalkylated pyrimidine subunits in a similar manner to that shown for the pyridine derivatives in chapter III.

Our approach was to investigate nucleophilic aromatic substitution of tetrafluoropyrimidine to produce mono-substituted derivatives which could, in principle, be used as heteroaromatic subunits in the synthesis of macrocyclic compounds bearing pyrimidine subunits.



Y = OMe, O^{t}Bu, $(CF_3)_2CF$
X = NMe, O

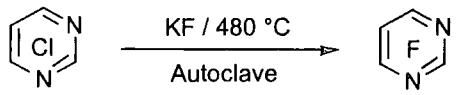
(Scheme 9)

Tetrafluoropyrimidine presents a different challenge to pentafluoropyridine in that the presence of an additional ring nitrogen atom makes tetrafluoropyrimidine considerably more reactive.

We begin by examining previous work involving tetrafluoropyrimidine, which includes several nucleophilic substitution reactions and demonstrates that this work is, in principle, achievable.

2) Tetrafluoropyrimidine.

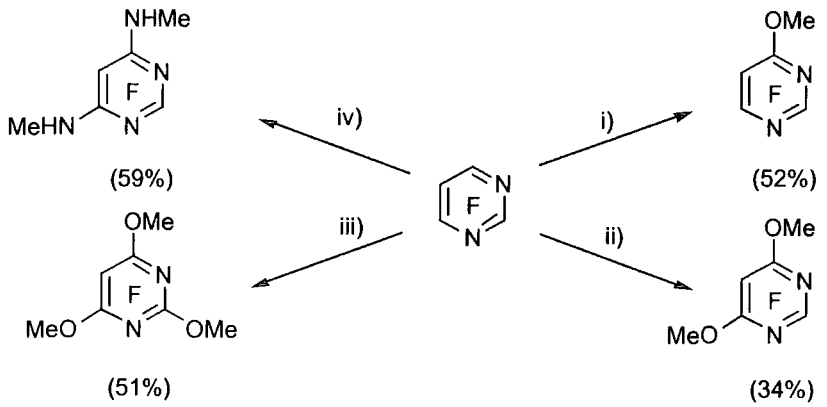
Tetrafluoropyrimidine is obtained from a reaction of tetrachloropyrimidine using alkali metal fluorides at high temperature in the absence of a solvent.[71]



(87%)

Tetrafluoropyrimidine is approximately 1000 times more reactive than pentafluoropyridine due to the highly activating influence of an additional ring nitrogen atom and there are several reported reactions involving nucleophilic aromatic substitution of tetrafluoropyrimidine.[71]

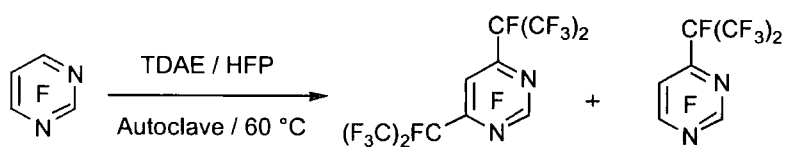
Banks, for example, has reported nucleophilic aromatic substitutions reactions of tetrafluoropyrimidine using a series of nucleophiles and in each case substitution occurs firstly at the 4- and 6-positions, with a third nucleophile entering at the 2-position.[72] This is consistent with the rules governing nucleophilic aromatic substitution in highly fluorinated aromatic systems detailed in chapter I.



Reagents and Conditions
i) 1 eq. NaOMe / MeOH ii) 2 eq. NaOMe / MeOH.
iii) 3 eq. NaOMe / MeOH iv) 2 eq. $MeNH_2$ / DMF

2.1) Perfluoroalkylation.

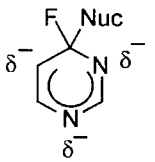
In our work, using the solvent-free perfluoroalkylation methodology described in chapter II, a reaction of HFP with TDAE in the presence of tetrafluoropyrimidine afforded two perfluoroalkylated products **(50)** and **(51)**.[73]



(50) (60%) **(51)** (10%)

Whereas a reaction of pentafluoropyridine with HFP occurs to give mainly the mono-substituted derivative **(1)**, and the bisperfluoroalklyated compound **(2)** as a minor

component, the more reactive tetrafluoropyrimidine system above, gave **(50)** as the major product, with the desired compound **(51)** being present in relatively small amounts. Unfortunately, attempts to increase the yield of **(51)** using a deficiency of HFP were unsuccessful, with **(50)** being the major product in all cases. This reflects the increased reactivity of **(51)** over tetrafluoropyrimidine, highlighting the highly activating influence of a perfluoroisopropyl group in this system and also the activating effects of two ring nitrogen atoms. The perfluoroisopropyl group is a very powerfully electron withdrawing substituent and renders the heteroaromatic ring in **(51)** more electron deficient than in tetrafluoropyrimidine and consequently, **(51)** is more susceptible to nucleophilic attack. The two ring nitrogen atoms are activating in both **(51)** and tetrafluoropyrimidine because of their ability to stabilise the carbanion intermediate in the transition-state (chapter I).

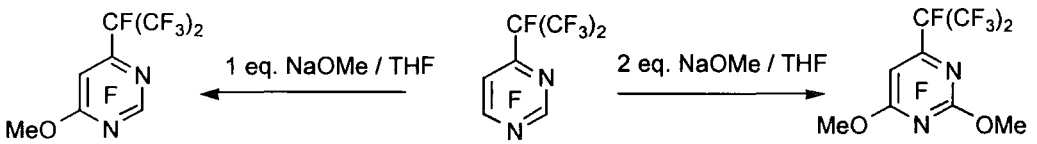


Charge stabilised by *ortho*- and *para*- nitrogen atoms

Although **(51)** was produced as a minor component and therefore, only small quantities were available, we were able to investigate several nucleophilic aromatic substitution reactions.

2.1.1) Reactions of (51).

Reactions of **(51)** with 1 and 2 equivalents of sodium methoxide gave the mono- and di-substituted compounds **(52)** and **(53)** respectively.

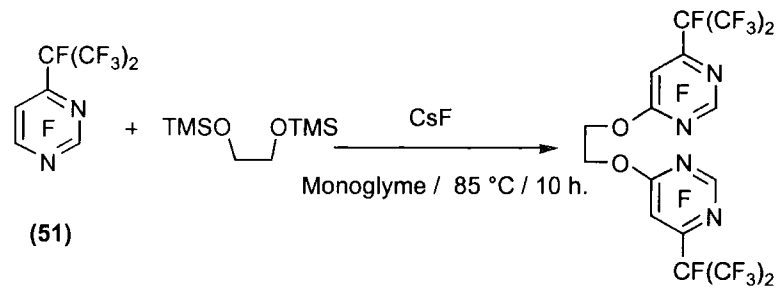


(52) (58%) **(51)** **(53)** (20%)

Substitution in **(51)** by the first methoxide nucleophile occurred at the 6-position, whereas a second substitution by methoxide occurs at the 2-position. This was confirmed by ^{19}F NMR spectroscopy which showed the disappearance of the higher frequency signals at –70.7 ppm and –48.3 ppm, corresponding to the 2- and 6-fluorine substituents in **(51)** respectively. The reduced yield of **(53)** compared to **(52)** suggests that a methoxy derivative has a deactivating influence on the pyrimidine ring system.

Therefore, in these model reactions we have demonstrated that **(51)** reacts as a difunctional electrophile in a manner similar to perfluoro-4-isopropylpyridine (chapter II) and consequently, the step-wise methodology for the synthesis of macrocycles (chapter III) should, in principle, also be applicable to the perfluoro-4-isopropylpyrimidine **(51)** system.

A reaction of **(51)** with ethylene glycol dianion afforded the bispyrimidyl species **(54)** in low yield. ^{19}F NMR spectroscopy confirmed that substitution had occurred at the 6-position in both heteroaromatic rings and was consistent with the substitution pattern in the model compound **(52)**.



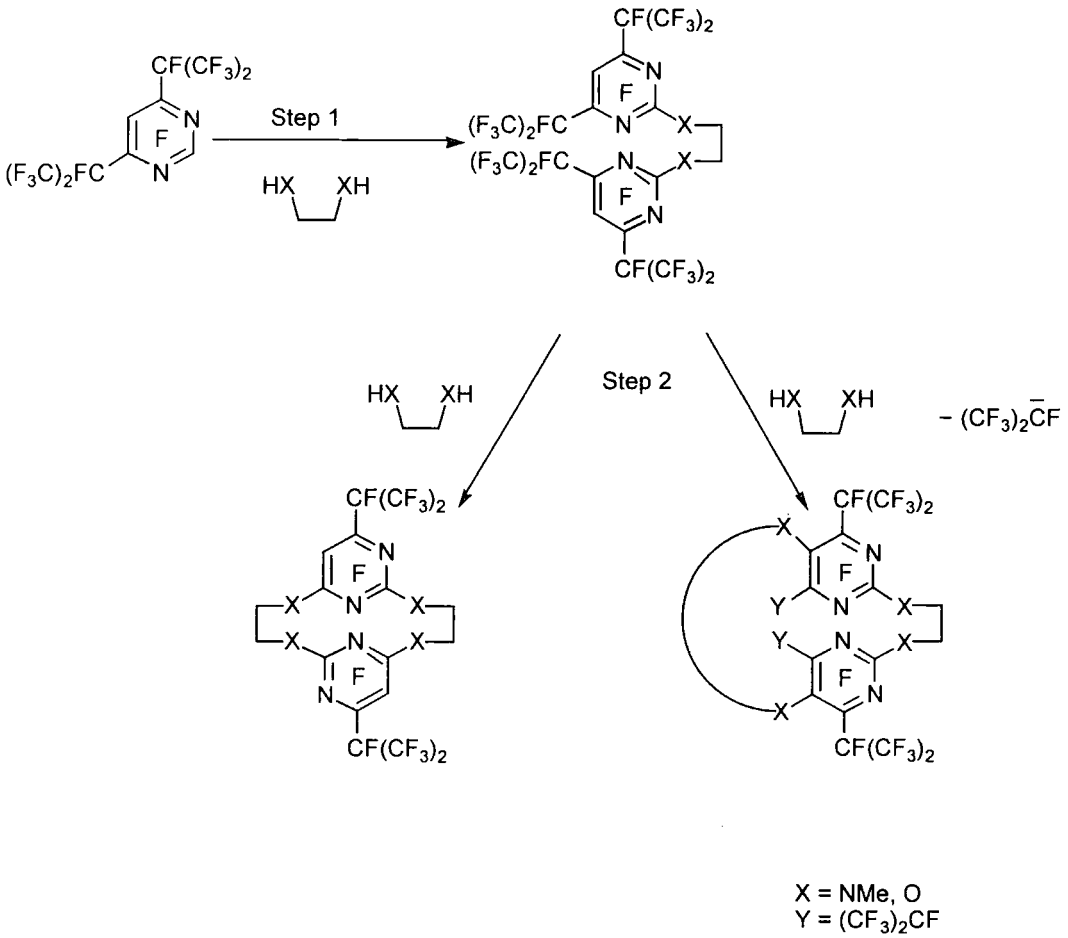
(51)

(54)
(20%)

A subsequent reaction of **(54)** with another equivalent of ethylene glycol dianion in the manner illustrated in scheme 9, gave a complex mixture of products which could not be identified.

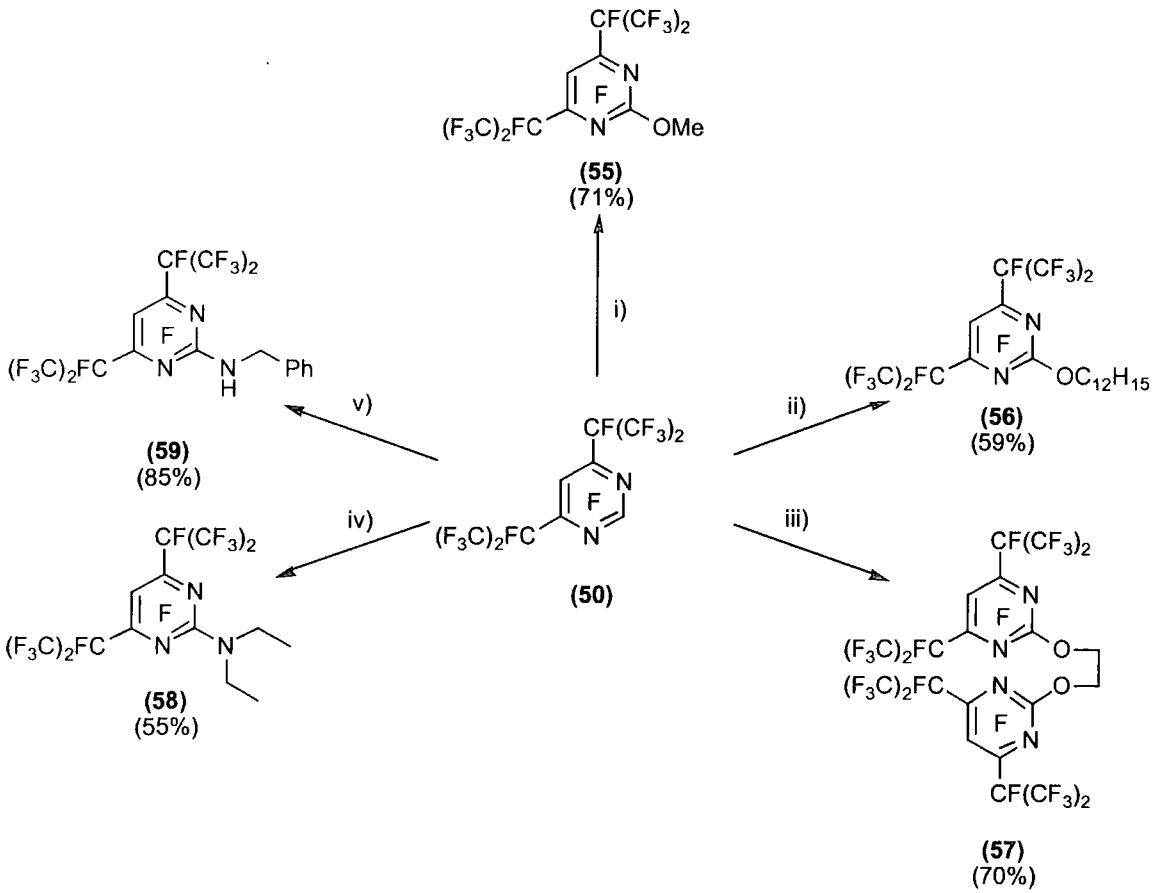
2.1.2) Reactions of (50).

We have also investigated the use of **(50)** as a possible precursor to macrocyclic compounds which can be envisaged by two conceivable processes: a) by nucleophilic displacement of one of the perfluoroalkyl groups, or b) by replacement of the 5-fluorine atom by a difunctional nucleophile, scheme 10. However we must first consider nucleophilic aromatic substitution in **(50)**.



(Scheme 10)

The bisperfluoroalkylated compound **(50)** reacts with a series of oxygen and nitrogen-centred nucleophiles to give the mono-substituted derivatives shown in scheme 11.



Reagents and Conditions
i) NaOMe / THF ii) NaH / 1-dodecanol iii) $TMSOCH_2CH_2OTMS$ / CsF / Diglyme
iv) Diethylamine / THF v) Benzylamine / THF

(Scheme 11)

In all cases substitution by the nucleophile occurs at the 2-position, *ortho-* to the two activating nitrogen atoms. This was established by ^{19}F NMR spectroscopy which showed the disappearance of the high frequency signal at –48.3 ppm which corresponds to the 2-fluorine atom. If substitution had occurred at the 5-position then this would have resulted in the disappearance of this signal at much lower frequency (–152.6 ppm) and this is clearly not the case here.

Only mono-substituted products could be obtained by reaction with either oxygen or nitrogen-centred nucleophiles and indeed the replacement of the 5-fluorine atom by a nucleophile could not be achieved even with an excess of regent at elevated temperatures (200 °C). Two possible explanations for this are: a) the relatively bulky perfluoroalkyl

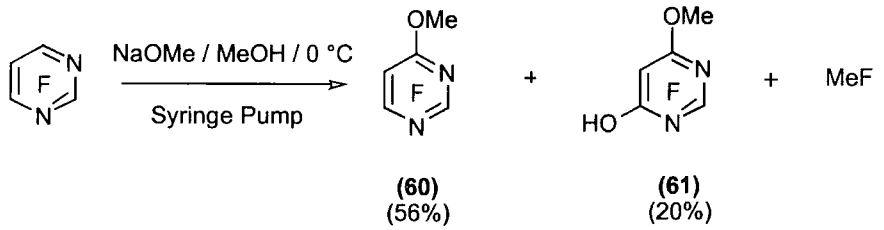
groups prevent a nucleophile from entering at the 5-position and b) the oxygen or nitrogen substituent at the 2-postion is destabilising to nucleophilic attack at the 5-position. Consequently, the bispyrimidyl species **(57)** could not be used as a precursor to a highly fluorinated macrocyclic compound as no further substitution could be achieved.

All of the compounds displayed in scheme 10 are highly soluble in perfluorocarbon liquids at room temperature.

2.2) Nucleophilic Substitution in Tetrafluoropyrimidine.

Although compound **(51)** could be a precursor to macrocyclic compounds in an analogous way to **(1)**, its low yield from the perfluoroalkylation reaction makes this an impractical starting material. Therefore, we investigated other mono-substituted pyrimidine derivatives for use as macrocyclic subunits, starting with a reaction of tetrafluoropyrimidine with sodium methoxide.

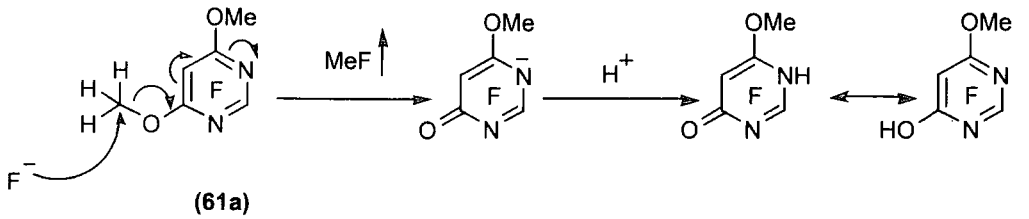
A carefully controlled reaction of sodium methoxide with tetrafluoropyrimidine at low temperature (0 °C) was carried out. In order to maximise the amount of mono-substituted product, a solution of sodium methoxide in methanol was added to an excess of tetrafluoropyrimidine over 6 hours via a syringe pump.



(60) (56%) **(61)** (20%)

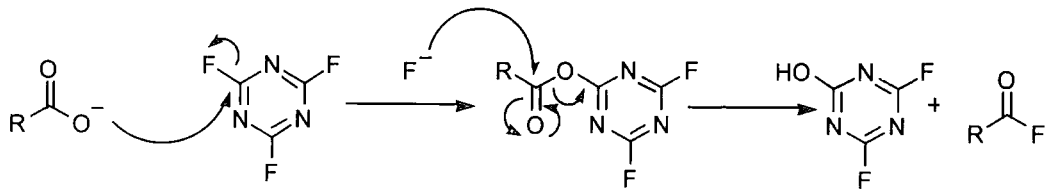
The methoxy-pyrimidine derivative **(60)** was produced in good yield with the hydroxy compound **(61)** as a side product, most likely formed from the fluoride ion induced demethylation of the 6-methoxy group in **(61a)**.

This can be rationalised by considering the pyrimidyl group as an excellent leaving group.

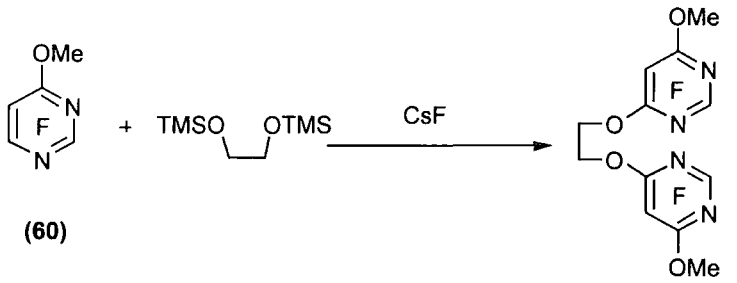


(61a)

A similar reaction has been reported by Olah in the trifluorotriazine system below, in which carboxylic acids are transformed into acid fluorides by nucleophilic substitution of trifluorotriazine followed by fluoride ion displacement of the nucleophile.[74]



A reaction of **(60)** with diethylene glycol dianion resulted in further nucleophilic substitution to give the bispyrimidyl species **(62)** in low yield along with numerous side products which made isolation of **(62)** difficult.



(60)

(62)
(14%)

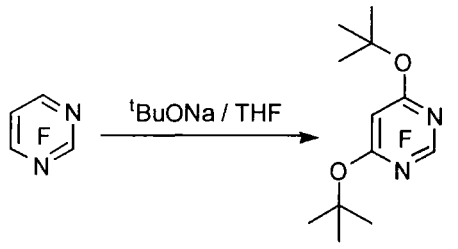
Despite the low yield for this reaction enough product was obtained for a second substitution reaction using diethylene glycol dianion, however this resulted in a complex mixture of products which could not be identified.

It is conceivable that attack by fluoride ion at the methyl group and the methylene site in the oxygen substituted derivative **(62)** is occurring due to the efficiency of the pyrimidine unit as a leaving group, resulting in the complexes mixtures we have

encountered so far in this series. Therefore, the low yields of the perfluoroalkylated derivatives **(53)** and **(54)** might also be explained by this demethylation process.

It should be possible however to introduce a group into a pyrimidine system where the above S_N2 process it less likely to occur, for example, a tertiary-butyl substituent.

A reaction of tetrafluoropyrimidine with sodium-tertiary-butoxide gave the disubstituted product **(63)** only, even at low temperatures.



(63)
(74%)

This approach appears to be successful in preventing the loss of the tertiary-butyl groups through the fluoride ion induced process observed for the methoxy derivatives above, however, only the di-substituted compound was obtained. This either reflects the increased reactivity of **(63)** over tetrafluoropyrimidine, or that a mono- substituted derivative is more soluble in the reaction media at the low temperatures used and thus it is more likely to undergo further nucleophilic attack.

3) Conclusions

In this series we have demonstrated that the perfluoroalkylation of tetrafluoropyrimidine occurs to give mainly bisperfluoroalkylated products, the desired mono-substituted compounds could not be produced in significantly useful quantities.

Nucleophilic substitution reactions in the perfluoroalkylated pyrimidine systems were investigated and demonstrated substitution at the 2- and 6- positions, no replacement of the 5-fluorine could be achieved.

Reaction of tetrafluoropyrimidine with methoxide gave mono-substituted derivatives, however, subsequent reactions of this compound resulted in complex mixtures and it has been suggested that demethylation by fluoride ion prevents further useful chemistry for this compound.

A reaction using a more sterically demanding system in order to prevent the demethylation process resulted in di-substituted products only.

In summary, tetrafluoropyrimidine is a highly reactive electrophile with gives mainly di-substituted products on reactions with nucleophiles and as such its use as a precursor to macrocyclic compounds in a similar manner to the pyridine system is limited.

Chapter V Polyfluoroalklyation Reactions Involving Trifluoromethyltrimethylsilane and Octafluorobut-2-ene.

1) Introduction.

In the previous chapters we have examined the chemistry of several heteroaromatic systems containing the perfluoroisopropyl substituent which were derived from reaction with HFP and fluoride ion. We demonstrated that the solvent free TDAE methodology described in chapter II could be used for the introduction of a perfluoroisopropyl group into both highly fluorinated pyridine and pyrimidine systems. In this chapter we present the chemistry of systems bearing two different perfluoroalkyl substituents, the trifluoromethyl group and the larger perfluoro-*sec*-butyl group. This work continues the overall theme of perfluoroalkylation reactions. In this chapter we hope to demonstrate that a variety of perfluoroalkyl groups can be introduced into highly fluorinated heteroaromatic systems and these systems can be explored further using nucleophilic substitution reactions.

Our approach was to first study the introduction of a CF_3 group into the pentafluoropyridine system using a powerful trifluoromethyl anion source, before examining the effect the introduction of this group has on subsequent nucleophilic aromatic substitution reactions. Next we aimed to develop a methodology for the introduction of a perfluoro-*sec*-butyl substituent using fluoride ion and octafluorobut-2-ene in an analogous way to that used for the perfluoro-4-isopropyl systems. The introduction of this group would result in the creation of a stereogenic centre within the molecule and the aim was to explore the effects this has on the system by attempting to synthesise and resolve diastereomers.

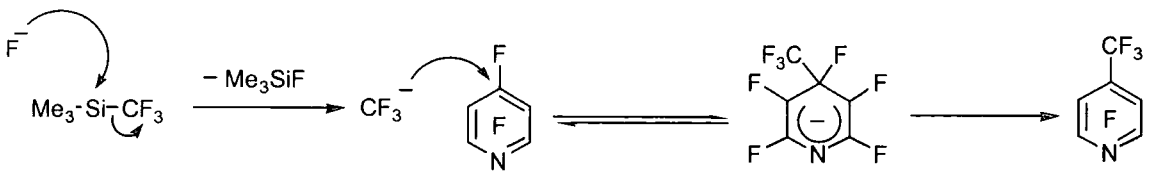
2) Perfluoroalkylation of Pentafluoropyridine.

2.1) Trifluoromethyltrimethylsilane.

Trifluoromethylated compounds have found a large number of industrial uses epecially as pharmaceutical and agro-chemicals because of the influence of the trifluoromethyl group in biologically active molecules and this is often associated with the increased lipophilicity that this substituent imparts.

Various methods for the introduction of a trifluoromethyl group have been established and have recently been reviewed.[75] Perhaps the most useful trifluoromethylating reagent is trifluoromethyltrimethylsilane, or Ruppert's reagent. This volatile liquid is the most widely used of a series of perfluoroalkylsilicon compounds the chemistry of which has been reviewed by Prakash.[76]

Ruppert's reagent can be considered as a source of trifluoromethyl-anion that is activated by a reaction with a suitable nucleophile (most commonly fluoride ion) which, can then be trapped using a range of electrophilic species[77-79], for example, pentafluoropyridine.

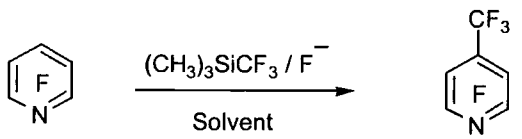


(64)

Although this reaction has been reported by Russian workers, the overall yields were relatively low (40%) and no further chemistry was described.[80]

We have conducted a series of reactions involving trifluoromethyltrimethylsilane with pentafluoropyridine using a variety of fluoride ion sources as activating nucleophiles for the generation of CF_3^- under different reaction conditions. The results are displayed in table 8. *Conversion* refers to the percentage of pentafluoropyridine that is transformed into **(64)** and was determined by a comparison of the appropriate integrals in the ^{19}F NMR spectrum.

General Procedure.



(64)

Table 8.

Nucleophile	Solvent	Temp / °C	Duration / h.	Conversion to (64) %
CsF	DMF	55	56	13[a]
KF	DMF	80	4	50
KF	DMF	80	20	40[b]
KF	DMF	100	20	50
KF	DMF	50	4	62
KF	DMF	45	4	10
KF	DMF	30	4	23
KF/CuBr	DMF	80	20	18
KF/CuBr	DMF	80	56	60[b]
CsF[c]	None	45	4	0[a]
CsF	None	20	20	0[a]
CsF	None	50	20	0[a]
CsF	MeCN	65	4	10[a]
CsF	MeCN	50	20	10[a]
CsF	DMSO	50	20	50[a]
CsF	DMSO	65	4	20[a]
CsF	Sulfolane	45	4	0[a]
TAS-F	THF	0	6	40[d]

a: numerous unknown side products produced; b: reaction carried out in autoclave; c: CsF coated in sulfolane; d: using same conditions reported by Yagupol'skii

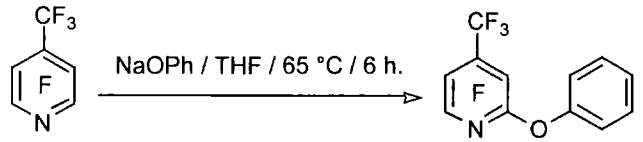
Firstly we investigated the effects of various solvents for the reaction and DMF was clearly shown to be a superior medium, with all other systems except the THF reaction giving complex mixtures of products for the above reaction.

The source of fluoride ion used was also an important factor, KF being a better source than CsF. However, using KF as the fluoride ion source for this reaction has limitations because its solubility in common organic solvents is low.

The reaction temperature and duration also had a significant effect on the efficiency of the reaction and a temperature of around 50 °C was the most effective with a duration of 4 hours. Longer reaction times either gave no additional increase in conversion, or indeed lower conversions were observed as more complex mixtures are produced.

In conclusion, our study demonstrates that KF as a fluoride ion source in DMF at 50 °C over 4 hours were the most effective reaction conditions for the synthesis of **(64)** using trifluoromethyltrimethylsilane. Unfortunately, the isolation of the products from the DMF reaction media proved extremely difficult because extraction into common organic solvents such as DCM was unsuccessful, as was extraction into perfluorocarbon liquids, reflecting the limited solubility of **(64)** in perfluorocarbon media. Distillation directly from the reaction medium did enable small amounts of **(64)** to be recovered, but the isolated yield was only 10%, although enough material was obtained to enable a nucleophilic substitution reaction to be investigated.

A reaction of **(64)** with sodium phenoxide gave the mono-substituted derivative **(65)** in good yield.

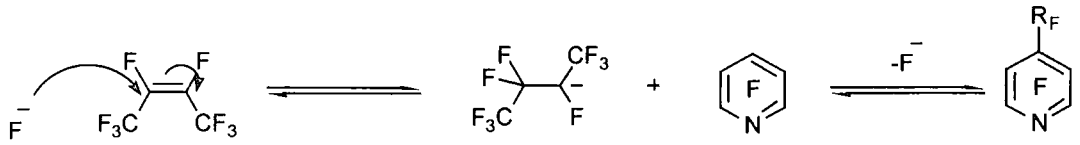


(65)
(77%)

This reaction demonstrates that further nucleophilic substitution in **(64)** is possible and therefore, the synthesis of multiply substituted derivatives containing the CF_3 moiety are, in principle, achievable. Unfortunately, difficulties in the isolation of **(64)** from the required reaction media make this an impractical starting material by this method.

2.2) Octafluorobut-2-ene.

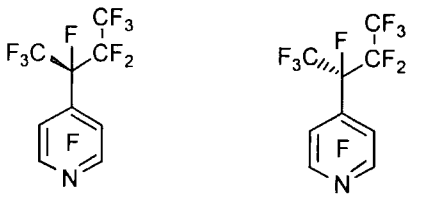
The reaction of octafluorobut-2-ene with pentafluoropyridine has been previously reported by Chambers and uses the fluoride ion induced negative Friedel Crafts chemistry described in chapter II.[81] Octafluorobut-2-ene reacts with fluoride ion to produce a fluorocarbanion which can subsequently be trapped using an electrophile, in this case pentafluoropyridine.



Octafluorobut-2-ene

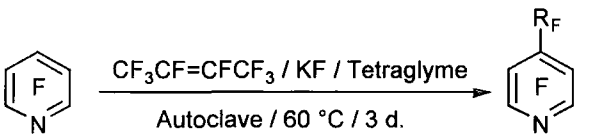
$R_F = CF_3CF_2(CF_3)CF$

The use of octafluorobut-2-ene presents a new aspect to the chemistry of the perfluoroalkyl groups we have seen so far, in that here a stereogenic centre is created within the perfluoroalkyl chain.



The two enantiomers for compound **(66)**

In this reaction the source of fluoride ion for the generation of the carbanion is anhydrous potassium fluoride and consequently dipolar aprotic solvents are required. In our work excellent yields for compound **(66)** were obtained.

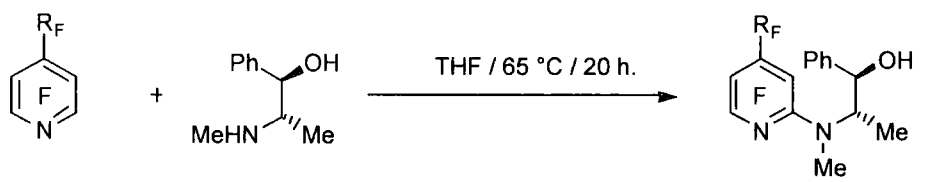


(66)
(71%)

$R_F = CF_3CF_2(CF_3)CF$

Although the solvent free methodology described in chapters II and IV could have been used, we chose the alkali metal fluoride method because the products could be recovered from the aprotic media by extraction into perfluorocarbon solvents, in which the perfluoroalkylated product **(66)** is highly soluble.

We attempted to resolve diastereomers of compound **(66)** using a homochiral nucleophile and a reaction of **(66)** with ephedrine resulted in nucleophilic substitution by nitrogen at the 2-position to give, we presume, a mixture of diastereomers.



Ephedrine

(67)
(65%)

$R_F = CF_3CF_2(CF_3)CF$

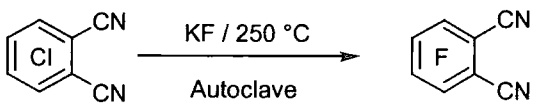
However, both the ^{19}F and ^{13}C NMR spectra for **(67)** were highly complex and we were unable to discriminate between the different diastereomers, also it was not possible to resolve the diastereomers using chromatography. This is likely a result of the relative distance between the two stereogenic centres within the molecule in that they are far enough apart as to produce very little stereochemical interaction.

3) Tetrafluorophthalonitrile.

Tetrafluorophthalonitrile is a fluorinated aromatic compound that is activated to nucleophilic attack at two adjacent sites by two *para-* nitrile substituents. It is therefore, an ideal molecule for the introduction of a chiral perfluoroalkyl group, as a second nucleophile would be anticipated to enter at the position adjacent to the first and the proximity of the two groups should maximise any stereochemical interactions. Firstly, before we consider this chemistry, a short discussion of some previous work with tetrafluorophthalonitrile is appropriate.

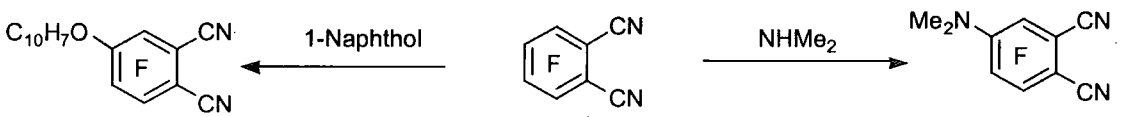
3.1) Introduction.

Tetrafluorophthalonitrile is a white solid which is obtained from tetrachlorophthalonitrile using KF in the absence of a solvent at high temperatures.[82]

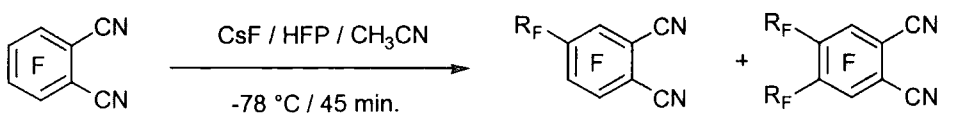


(72%)

It readily undergoes nucleophilic aromatic substitution reactions, for example, Haszeldine has investigated reactions of tetrafluorophthalonitrile with simple nucleophiles to give mono-substituted derivatives.[82]



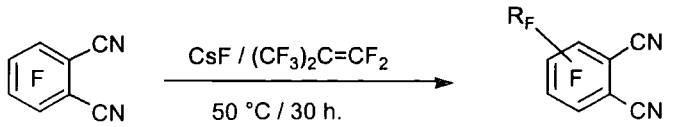
Perfluoroalkylation of tetrafluorophthalonitrile using HFP has been recently reported by Gorun and showed the introduction of two perfluoroisopropyl groups adjacent to one another at the 4- and 5-positions.[83]



$R_F = (CF_3)_2CF$

(43%) (43%)

Perfluoroalkylation using the highly reactive fluorinated alkene, perfluoroisobutene has been demonstrated by Russian workers, but, the regiochemistry of the products is not clear.[84]



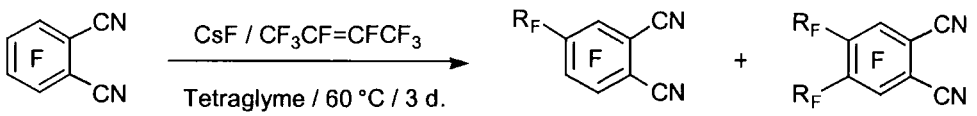
$R_F = (CF_3)_3C$

There is a great deal of interest in the chemistry of phthalonitriles because they are known precursors to phthalocyanines, an important class of molecules with a wide range of applications, from catalysts to solid state materials and dyes. Indeed the use of highly fluorinated phthalocyanines have been investigated for the treatment of tumours in mice.[85]

Our approach was to investigate the nucleophilic perfluoroalkylation of tetrafluorophthalonitrile using octafluorobut-2-ene, which will now be described.

3.2) Perfluoroalkylation using Octafluorobut-2-ene.

A reaction of octafluorobut-2-ene with tetrafluorophthalonitrile gave a mixture of mono- and di-substituted products.



(68) (14%) **(69)** (53%)

$R_F = CF_3CF_2(CF_3)CF$

As with the tetrafluoropyrimidine system in chapter IV, the desired mono-substituted product was difficult to obtain without a significant proportion of the bisperfluoroalklyated compound **(69)** being produced. This reflects the increased reactivity of **(68)** over tetrafluorophthalonitrile because of the highly activating influence of a perfluoroalkyl group (see chapter IV).

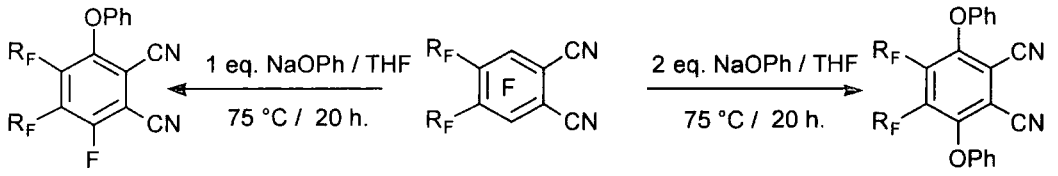
The perfluoroalkylated compounds **(68)** and **(69)** are both highly soluble in perfluorocarbon solvents, and their isolation from the tetraglyme reaction mixture was made simple by extraction into perfluoromethylcyclohexane.

Confirmation of the regiochemistry in **(68)** comes from the ^{19}F NMR spectrum. The two trifluoromethyl groups are clearly assigned to the peaks at –72.1 and –80.3 ppm, whereas the two complex patterns at and –80.5 and –85.5 ppm correspond to the 3- and 5-fluorine atoms respectively. In both cases the peaks are complex and broadened due to the rapid rotation of the perfluoroalkyl group. Assignments for the fluorine atoms of the CF_2 group of the perfluoroalkyl substituent is very difficult and a series of complex overlapping signals are observed which also contain the signal for the 6-fluorine atom. Thus we have established from the ^{19}F NMR spectrum that the introduction of the perfluoro-*sec*-butyl group in tetrafluorophthalonitrile enters at the 4-position giving compound **(68)**. This is consistent with previous work in the area of tetrafluorophthalonitrile chemistry and also with the expected orientation of substitution by minimising the number of *para*- fluorine atoms (chapter I).

For **(69)**, evidence that the second perfluoroalkyl group enters adjacent to the first at the 5-position also comes from the ^{19}F NMR spectrum. Again the two different CF_3 groups of the perfluoroalkyl substituents are observed at –73.5 and –80.6 ppm respectively. The fluorine atoms at the 3- and 6-positions give rise to a resonance at –84.9 and –88.5 ppm and show the correct integration for two fluorine atoms. Two signals are observed due to rapid rotation about each perfluoroalkyl group in a similar manner to that observed for the perfluoroisopropyl group outlined in chapter II. Also, two distinct signals for each rotamer for the tertiary fluorine of the perfluoro-*sec*-butyl group are also observed confirming this explanation. It is unlikely that the presence of two signals for the same fluorine atoms are due to the different diastereomers because the same effect is observed in compound **(68)**, which is present as a pair enantiomers.

Since the desired compound **(68)** was present in only small amounts it was impractical to begin studies on the separation of diastereomers of **(68)** using a homochiral nucleophile, instead we chose to investigate nucleophilic aromatic substitution in **(69)** and attempted to replace all of the remaining fluorine atoms.

A reaction of **(69)** with both 1 and 2 equivalents of sodium phenoxide produced the mono- and di-substituted derivatives **(70)** and **(71)** respectively.



(70) (47%)

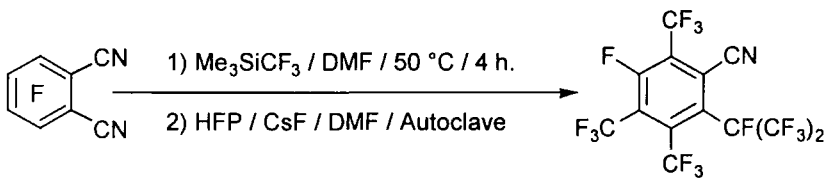
(71) (37%)

$R_F = CF_3CF_2(CF_3)CF$

This reaction demonstrates that highly substituted aromatic compounds can be derived from highly fluorinated starting materials using nucleophiles.

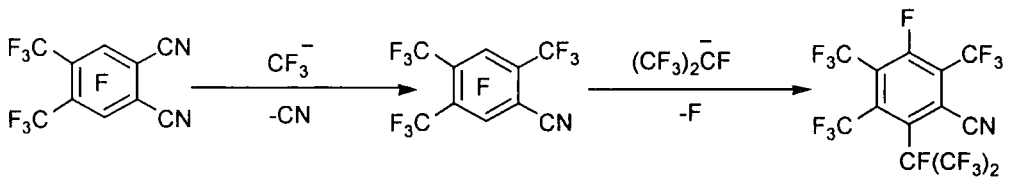
Finally in this series a reaction of tetrafluorophthalonitrile with two different perfluoroalkylating agents was carried out with the aim to produce highly fluorinated precursors to phthalocyanines that would be soluble in perfluorocarbon liquids.

Tetrafluorophthalonitrile was reacted with trifluoromethyltrimethylsilane using the procedure developed above (section 2.1). Again, the isolation of the products from the DMF solvent required was difficult and therefore, a second perfluoroalkyl group was introduced into the molecule using a reaction with HFP and fluoride ion (chapter II). This rendered some of the products from the reaction soluble in fluorocarbon liquids and isolation of the product mixture was possible by extraction into perfluoromethylcyclohexane. However, the reaction mixture was highly complex and purification of the major product **(72)** was difficult, although, column chromatography did enable a very small amount of the highly substituted compound **(72)** to be recovered, which was subsequently identified from its x-ray crystal structure.

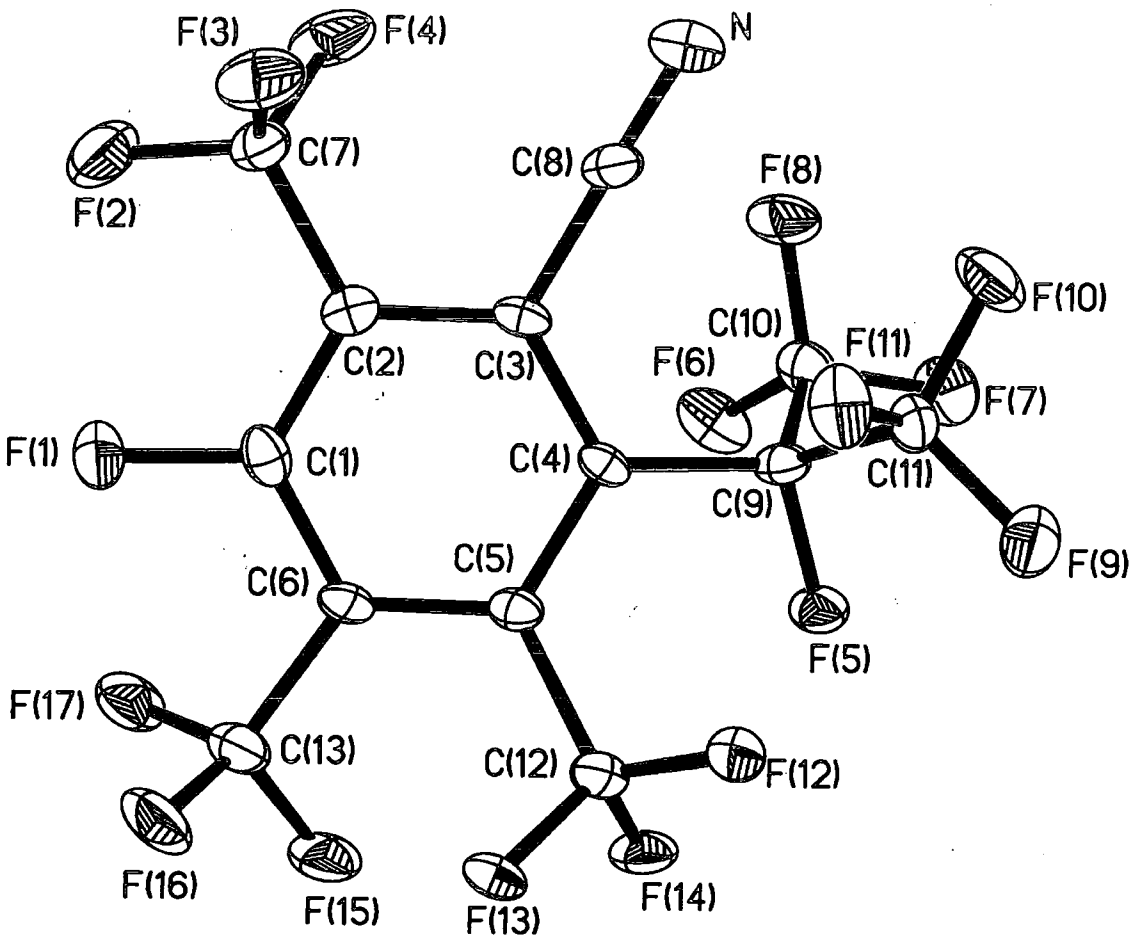


(72)

In this reaction several of the ring fluorine atoms have been replaced in addition to one of the nitriles groups which is likely to have been replaced by a CF_3 substituent.



(72)


F(3)
F(4)
N
C(7)
C(8)
F(8)
F(2)
F(10)
C(10)
F(11)
C(2)
C(3)
F(6)
F(7)
F(1)
C(1)
C(4)
C(11)
C(9)
F(9)
C(5)
C(6)
F(5)
F(17)
C(13)
C(12)
F(12)
F(16)
F(15)
F(13)
F(14)

Compound (72)

4) Conclusions

The introduction of a trifluoromethyl group into the pentafluoropyridine system proceeds with reasonable conversion using DMF as the reaction medium in the presence of KF. Unfortunately, the isolation of the product mixture from this system is very difficult making this an impractical method for the synthesis of perfluoro-4-methylpyridine as a starting material.

The introduction of a perfluoro-*sec*-butyl group into the pentafluoropyridine system is possible by a fluoride ion induced polyfluoroalkylation using octafluorobut-2-ene, and unlike the solvent free methodology described in chapter II and IV this reaction uses an alkali metal fluoride in an aprotic solvent to induce reaction. The perfluoro-*sec*-butyl group has a stereogenic centre, but we were unable to resolve diastereomers of this compound using a homochiral nucleophile.

The tetrafluorophthalonitrile system was used for the introduction of a perfluoro-*sec*-butyl group in a similar manner to the pyridine system to give mono- and di-substituted products. However further studies regarding the stereochemistry of such compounds were not carried out because of the difficulty in producing only mono-substituted derivatives, although some nucleophilic substitution reactions were investigated.

Chapter VI Experimental.

1) Instrumentation.

Reagents and Solvents

All chemicals were supplied by Aldrich or Fluorochem unless otherwise stated, tetrafluorophthalonitrile was kindly provided by Dr. Wang Shu-Zhong. All solvents were dried according to literature methods. Potassium fluoride was flame dried and stored under vacuum at high temperature, Caesium fluoride was dried under vacuum at 250 °C. Column chromatography was performed using silica gel supplied by Fluorochem.

Gas Liquid Chromatography

Chromatographic analyses were performed on a Hewlett Packard 5890 Series II gas liquid chromatograph equipped with a 25 m cross-linked methyl silicone capillary column with a flame ionisation detector.

Elemental Analysis

Carbon, hydrogen and nitrogen analysis were obtained using an Exeter Analytical CE-440 Elemental Analyser.

NMR Spectroscopy

^{1}H and spectra were obtained from a Varian VXR400 Spectrometer (400 MHz). ^{19}F spectra were recorded on the Varian Spectrometer (376 MHz) and ^{13}C at (100 MHz). All spectra were obtained using TMS and/or $CFCl_3$ as an internal reference. J values are given in Hertz.

Mass Spectroscopy

Mass spectra were obtained from a VG Trio 1000 Mass spectrometer (electronic ionisation) coupled to a GLC as above. Accurate mass determinations were performed on a Micromass Autospec Mass Spectrometer. Macrocycle binding studies were performed on a Micromass LCT spectrometer.

IR Spectra

Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR using KBr discs or thin film liquid between KBr plates.

2) Experimental to Chapter II.

Synthesis of Perfluoro-4-isopropylpyridine (1).

A stainless steel autoclave (1000 ml) was charged with pentafluoropyridine (200 g, 1.2 mol) and tetrakis(dimethylamino)ethene (TDAE) (0.45 g, 2.0 mmol), under an atmosphere of dry nitrogen. Hexafluoropropene was transferred to the autoclave under vacuum before the autoclave was sealed and heated to 60 °C over 20 h. The autoclave contents were then cooled and opened under vacuum, no gases were recovered. The contents were transferred to a round bottomed flask and distillation atmospheric pressure, gave *perfluoro-4-isopropylpyridine* **(1)** as a colourless liquid (230 g, 60%); bp 129°C; (Found C, 29.8; N, 4.2. $C_8F_{11}N$ requires C, 30.1; N, 4.4%).

Synthesis of 3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (3).

A mixture containing, sodium methoxide (4.1 g, 70 mmol), perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) and methanol (15 ml) was heated to reflux over 72 h before being cooled to room temperature and water (15 ml) added. Extraction into DCM (2 x 30 ml), enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane/DCM, 6:1) gave *3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(3)** as a colourless solid (1.7 g, 75%); Rf, 0.20; mp 47-48 °C; (Found C, 37.4; N, 3.72; H, 2.71. $C_{11}H_9F_8NO_3$ requires C, 37.2; N, 3.90; H, 2.50%).

Synthesis of 3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (4).

Sodium metal (1.7 g, 60 mmol) was added to a solution of phenol (6.6 g, 60 mmol) in THF (20 ml) and stirred over 1 h at room temperature, perfluoro-4-isopropylpyridine **(1)** (3g, 10 mmol) was then added dropwise. The mixture was heated to reflux over 72 h before being cooled to room temperature and water (15 ml) added. Extraction into DCM (2 x 30 ml), enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane/DCM, 6:1) gave *3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(4)** as a white solid (0.91 g, 27 %); Rf, 0.25; mp 47-48 °C; (Found C, 57.4; N, 2.6; H, 2.8. $C_{26}H_{15}F_8NO_3$ requires C, 57.6; N, 2.6; H, 2.8%).

Synthesis of 2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (5).

Butyllithium (6.3 mmol) was added dropwise *via* syringe over 1 h to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in diethyl ether (15 ml) at -78°C under an atmosphere of dry nitrogen. After being stirred at -78 °C for 45 minutes, ethanol (5 ml) was added followed by water (15 ml). Extraction into DCM (2 x 30 ml), enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane/DCM, 6:1) afforded *2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(5)** as a colourless liquid (1.3 g, 58%); Rf, 0.35; bp 177 °C; (Found C, 41.1; N, 2.7; H, 3.9. $C_{12}H_9F_{10}N$ requires C, 40.5; N, 2.7; H, 3.9%).

Synthesis of 2,6-dibutyl-3,5,-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (6).

Butyllithium (12.0 mmol) was added dropwise *via* syringe over 1 h to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in diethyl ether (15 ml) at -78°C under an atmosphere of dry nitrogen. After being stirred at -78°C for 45 minutes, ethanol (10 ml) was added followed by water (15 ml). Extraction into DCM (2 x 30 ml), enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *2,6-dibutyl-3,5,-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(6)** as a colourless liquid (0.5 g, 20%); Rf, 0.25; bp 232 °C; (Found C, 48.5; N, 3.50; H, 4.84. $C_{16}H_{18}F_9N_1$ requires C, 48.6; N, 3.54; H, 4.56%).

Synthesis of 6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (7).

Tertiary-butylmagnesium chloride (6.3 mmol) was added slowly to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in THF (15 ml) under an atmosphere of dry nitrogen. The mixture was stirred slowly for 5 hours at -15 °C before ethanol (5 ml) and dilute HCl (15 ml) were added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (eluent hexane, R_f: 0.28) gave *6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(7)** as a colourless liquid; (0.28 g, 41%); Rf, 0.28; bp 178 °C; (Found C, 40.6; H, 2.54; N, 3.84, $C_{12}H_9F_{10}N_1$ requires C, 40.3; H, 2.54; N, 3.84%).

Synthesis of 2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (8).

Tertiary-butyllithium (50 mmol) was added to a suspension of $Cu^{(I)}Br$ (3.6 g, 25 mmol) in diethyl ether (20 ml) at -41 °C under an atmosphere of dry nitrogen. The mixture was stirred at -41 °C for 30 min before perfluoro-4-isopropylpyridine **(1)** (6.0 g, 20 mmol) was added slowly *via* syringe. The mixture was stirred over 6 h before dilute HCl (5 ml) was added. The mixture was filtered through a No. 3 sinter and water (20 ml) added. Extraction of the filtrate into DCM (2 x 20 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography on silica gel (hexane) gave *2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(8)** as a yellow oil (1.1 g, 16%); Rf, 0.30. Compound decomposition prevented analysis.

Synthesis of 4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione (9).

Sodium hydride (0.52 g, 13 mmol) was washed with hexane before diethylmalonate (2.1 g, 13 mmol) was added slowly, the mixture was then stirred for 1 hour at 0 °C under an atmosphere of dry nitrogen. Perfluoro-4-isopropylpyridine **(1)** (4 g, 13 mmol) in THF (20 ml) was added slowly using a dropping funnel and the mixture was then stirred over 5 h, before water (5 ml) was added Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (DCM/Hexane 1:1) gave diethyl *4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5dione* **(9)** as a clear liquid (2.9 g, 49%); Rf, 0.41; bp 274 °C; (Found C, 38.9; H, 2.20; N, 3.07. $C_{15}H_{11}F_{10}NO_4$ requires C, 39.2; H, 2.40; N, 3.05%).

Synthesis of 6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (10).

1-Propenylmagnesium bromide (9.4 mmol) was added *via* syringe to a stirred solution of perfluoro-4-isopropylpyridine **(1)** (3.0 g, 9.4 mmol) in THF (20 ml) under an atmosphere of dry nitrogen. The solution was then heated under reflux over 20 h before dilute HCl (15 ml) was added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(10)** as colourless oil (2.2 g, 69%);

Rf, 0.40; bp 186 °C; (Found C, 38.5; H, 1.38; N, 4.04. $C_{11}H_5F_{10}N$ requires C, 38.7; H, 1.47; N, 4.11%).

Synthesis of 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (11).

Phenylmagnesium chloride (12.5 mmol) was added to a solution of perfluoro-4-isopropylpyridine (1) (2.0 g, 6.3 mmol) in THF (20 ml) under an atmosphere of dry nitrogen. The solution was heated under reflux over 24 h before being cooled to room temperature and dilute HCl (15 ml) added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave a mixture of 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine and biphenyl. This mixture was dissolved into acetone and extraction using perfluoromethylcyclohexane followed by removal of the solvent on a rotary evaporator gave *2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(11)** as a white solid (0.5 g, 21%); Rf, 0.38; mp 43-45 °C; (Found C, 44.2; H, 1.40; N, 3.71. $C_{14}H_5F_{10}N$ requires C, 44.6; H, 1.33; N, 3.71%).

Synthesis of 3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (12).

Phenylmagnesium bromide (30 mmol) was added *via* syringe to a solution of perfluoro-4-isopropylpyridine **(1)** (3.0 g, 9.4 mmol) in THF (15 ml) under an atmosphere of dry nitrogen. The solution was heated under reflux over 20 h before being cooled to room temperature and dilute HCl (15 ml) added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(12)** as a white solid (1.9 g, 47%); Rf, 0.24; mp 56-57 °C; (Found C, 55.2; H, 2.24; N, 3.16. $C_{20}H_{10}F_9N$ requires C, 55.2; H, 2.30; N, 3.22%).

Synthesis of 2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (13).

1-Propynylmagnesium bromide in THF (9.4 mmol) was added *via* syringe to a stirred solution of perfluoro-4-isopropylpyridine **(1)** (3.0 g, 9.4 mmol) in THF (20 ml) under an atmosphere of dry nitrogen. The solution was then heated under reflux over 20 h before dilute HCl (15 ml) was added. Extraction in DCM (2 x 15 ml) enabled recovery of

organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) followed by sublimation under vacuum gave *2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(13)** as a white solid (1.9 g, 61%); Rf, 0.44; mp 61-62 °C; (Found C, 38.6; H, 0.87; N, 4.10. $C_{11}H_3F_{10}N$ requires C, 38.9; H, 0.88; N, 4.1%).

Synthesis of 2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (14).

1-Propynylmagnesium bromide (30 mmol) was added *via* syringe to a stirred solution of perfluoro-4-isopropylpyridine **(1)** (3.0 g, 9.4 mmol) in THF (20 ml) under an atmosphere of dry nitrogen. The solution was then heated under reflux for 20 h before dilute HCl (25 ml) was added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) followed by sublimation under vacuum gave *2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(14)** a white solid (1.4 g, 41%); Rf, 0.35; mp 103-104 °C; (Found C, 46.5; H, 1.71; N, 3.87. $C_{11}H_5F_{10}N$ requires C, 46.8; H, 1.47; N, 3.90%).

Synthesis of 3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (15).

2,3,5-Trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(13)** (1.1 g, 3.2 mmol) was added to a solution of sodium methoxide (0.22 g, 4.0 mmol) in methanol (20 ml). The mixture was then heated to reflux over 3 h before being cooled to room temperature and water (15 ml) added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(15)** as a white solid (1.1 g, 60%); Rf, 0.40; mp 67-68 °C; (Found C, 41.3; H, 2.0; N, 3.8. $C_{13}H_6F_9N$ requires C, 41.0; H, 1.7; N, 3.9%).

Synthesis of diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (18).

Diethylamine (0.9 g, 12.6 mmol) was dropwise to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in THF (10 ml). The mixture was then heated to reflux for 20 h before being cooled to room temperature and dilute HCl added (15 ml). Extraction into DCM (2 x 15 ml) enabled recovery of organic products. Extraction in

DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine* **(18)** as a colourless liquid (2.1 g, 92 %); Rf, 0.28; bp 212-214 °C; (Found C, 38.7; H, 2.55; N, 7.50. $C_{12}H_{10}F_{10}N_2$ requires C, 38.7; H, 2.69; N, 7.53%).

Synthesis of {6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}diethylamine (19).

Diethylamine (2.8 g, 40 mmol) was dropwise to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in THF (10 ml). The mixture was then heated to reflux over 4 d before being cooled to room temperature and dilute HCl added (25 ml). Extraction into DCM (2 x 15 ml) enabled recovery of organic products. Extraction into DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane), gave *{6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}diethylamine* **(19)** as a colourless liquid (0.94 g, 40%); R_f, 0.28; bp 262-263 °C; (Found C, 44.7; H, 4.6; N, 9.8. $C_{16}H_{20}F_9N_3$ requires C, 45.1; H, 4.7; N, 9.8%).

Synthesis of benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine (20).

Benzylamine (2.0 g, 12.6 mmol) was dropwise to a solution of perfluoro-4-isopropylpyridine **(1)** (2.0 g, 6.3 mmol) in THF (10 ml). The mixture was then heated to reflux over 30 min before being cooled to room temperature and dilute HCl added (15 ml). Extraction into DCM (2 x 15 ml) enabled recovery of organic products. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine* **(20)** as a colourless liquid (1.8 g, 74 %); Rf, 0.35; bp 243-244 °C; (Found C, 44.4; H, 1.89; N, 5.95. $C_{15}H_8F_{10}N_2$ requires C, 44.3; H, 1.97; N, 5.90%).

3) Experimental to Chapter III.

Synthesis of 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)pyridine (34).

A mixture of 1,1-dimethyl-1-silaethoxy-1,1-dimethyl-1-silaethane (3 g, 14 mmol), dried CsF (2.0 g, 13 mmol) and perfluoro-4-isopropylpyridine (1) (10 g, 30 mmol), in anhydrous monoglyme (75 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2 x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Reduced pressure distillation gave *3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)pyridine* **(34)** (11 g, 94%); bp 120 °C (5 mbar).

Synthesis of 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene (35).

A mixture of 1,1-dimethyl-1-silaethoxy-1,1-dimethyl-1-silaethane (0.35 g, 1.7 mmol), dried CsF (0.5 g, 3.2 mmol) and 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoromethyl)ethyl]-2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy)pyridine **(34)** (2.5 g, 3.8 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 4:1) gave a white solid which after recrystallisation from toluene three times gave *19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene* **(35)** (43%, 0.5 g); mp 191-194 °C; (Found C, 35.4; H, 1.20; N,4.11; $C_{20}H_8F_{18}N_2$ requires, C, 35.2; H, 1.18; N, 4.11%).

Synthesis of 2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-6-[2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy]pyridine(36).

A mixture containing 2-(1,1-dimethyl-1-silaethoxy)-1-[2-(1,1-dimethyl-1-silaethoxy)ethoxy]ethane (4.3 g, 15 mmol), dried CsF (0.6 g, 3.9 mmol) and perfluoro-4-isopropylpyridine **(1)** (15 g, 40 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 1 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2 x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatgrpghy (hexane/diethyl ether 5:1) gave *2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-6-[2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy]pyridine* **(36)** as a colourless liquid (18 g, 64%) bp >300 °C.

Synthesis of 25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene (37).

A mixture of 2-(1,1-dimethyl-1-silaethoxy)-1-[2-(1,1-dimethyl-1-silaethoxy)ethoxy]ethane (0.6 g, 2.0 mmol), dried CsF (0.6 g, 3.9 mmol) and 2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-6-[2-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethoxy]pyridine (36) (3 g, 4.3 mmol), in anhydrous monoglyme (600 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 5:1) gave a yellow solid, which after recrystallisation from toluene three times gave *25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene* **(37)** (0.62 g, 40%); mp; 201-204 °C; (Found C, 37.5; H, 2.00; N, 3.64; $C_{24}H_{16}F_{18}N_2O_6$ requires C, 37.4; H, 2.09; N, 3.64%).

Synthesis of 2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (38).

A mixture of 1,1-dimethyl-1-silaethoxy-1,1-dimethyl-1-silaethane (7.6 g, 28 mmol), dried CsF (3.0 g, 20 mmol) and perfluoro-4-isopropylpyridine (1) (20 g, 60 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added which precipitated the crude product. The crude product was recovered by filtration and recrystallisation from toluene gave *2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine* **(38)** as a white solid (19 g, 90%); mp 160-162 °C; (Found C, 38.3; H, 0.83; N, 3.88 $C_{23}H_6F_{20}N_2O_2$ requires C, 38.2; H, 0.83; N, 3.88%).

Synthesis of 26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene (39).

A mixture of 1-[5-(1,1,-dimethyl-1-silaeoxy)-3-methylphenoxy]-1,1-dimethyl-1-silaethane (1.1 g, 3.8 mmol), dried CsF (1.3 g, 8.5 mmol) and 2,3,5-trifluoro-6-(5-methyl-3-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}phenoxy)-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (38) (3 g, 5.8 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 5:1) gave a yellow solid, which after recrystallisation from toluene three times gave *26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene* **(39)** (1.0 g, 33%); mp; 201-204 °C; (Found C, 44.6; H, 1.71; N, 3.47; $C_{30}H_{12}F_{18}N_2O_4$ requires C, 44.7; H, 1.50; N, 3.47%).

Synthesis of methyl[2-methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]2-pyridyl)}amine (40).

A mixture containing N,N'dimethylethylenediamine (1.4 g, 17 mmol) and perfluoro-4-isopropylpyridine (1) (10 g, 30 mmol), in anhydrous THF (75 ml) was heated to 75 °C under an atmosphere of dry nitrogen. The mixture was heated over 1 d before being allowed to cool to room temperature and sodium hydrogen carbonate solution (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Reduced pressure distillation gave *methyl[2-methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]2-pyridyl)}amine* **(40)** (11 g, 94%); bp 140 °C (5 mbar).

Synthesis of 2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10,(20),15,17-hexaene (41).

A mixture of N,N'dimethylethylenediamine (0.2 g, 2.3 mmol), dried CsF (0.5 g, 3.2 mmol) and methyl[2-methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]2-pyridyl)}amine (40) (3.0 g, 4.3 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and sodium hydrogen carbonate solution (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 4:1) gave a white solid, which after recrystallisation from toluene four times gave *2,5,11,14,19,20-hexaaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetramethyltricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10,(20),15,17-hexaene* **(41)** (0.23 g, 14%); mp. 200-202 °C; (Found C, 39.1; H, 2.73; N, 1.46; $C_{24}H_{20}F_{18}N_6$ requires C, 39.3; H, 2.75; N, 11.4%).

Synthesis of 11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20), 15, 17-hexaene (42).

A mixture of 1,1-dimethyl-1-silaethoxy-1,1-dimethyl-1-silaethane (0.4 g, 1.9 mmol), dried CsF (0.5 g, 3.2 mmol) and methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (40) (3 g, 4.4 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 5:1) gave a yellow solid, which after recrystallisation from toluene three times gave *11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20), 15, 17-hexaene* **(42)** (0.27 g, 20%) as a white solid; mp 208-209 °C; (Found C, 37.1; H, 1.95; N, 7.78; $C_{22}H_{14}F_{18}N_4O_2$ requires C, 37.3; H, 1.99; N, 7.91%).

Synthesis of 2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene (43).

A mixture of 2-(1,1dimethyl-1-silaethoxy)-1-[2-(1,1-dimethyl-1-silaethoxy)ethoxy]ethane (0.7 g, 4.4 mmol), dried CsF (0.6 g, 3.9 mmol) and methyl[2-(methyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amino)ethyl]{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}amine (40) (3 g, 4.4 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 5:1) gave a yellow solid, which after recrystallisation from toluene three times gave *2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene* **(43)** (0.42 g, 20%); mp 207-210 °C; (Found C, 38.8; H, 2.53; N, 7.61; $C_{24}H_{18}F_{18}N_4O_3$ requires C, 38.3; H, 2.41; N, 7.45%).

Synthesis of 2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol (44a).

A mixture containing ethanolamine (2.9 g, 33.0 mmol) and perfluoro-4-isopropylpyridine (**1**) (15 g, 50 mmol) in THF (30 ml) was heated to 70 °C over 16 hours before being cooled and a saturated solution of aqueous sodium hydrogen carbonate (30 ml) added. Extraction into DCM (2-x 50 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Distillation under reduced pressure gave *2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol* **(44a)** (10 g, 87%); bp 50 °C (5 mbar); (Found, C, 33.1; H, 1.67; N, 7.80; $C_{10}H_6F_{10}N_2O$ requires C, 33.4; H, 1.68; N, 7.80%).

Synthesis of {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine (44).

A mixture containing sodium hydride (1.4 g, 58 mmol), perfluoro-4-isopropylpyridine (15 g, 47 mmol) and 2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol **(44a)** (10 g, 29 mmol) in THF (30 ml) was heated to 70 °C over 16 h under an atmosphere of dry nitrogen before being cooled and water (30 ml) added. Extraction into DCM (2-x 50 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Distillation under reduced pressure *gave {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine* **(44)** (16 g, 52%); bp 140 °C (0.1 mbar); (Found, C, 32.4; H, 0.74; N, 6.40; $C_{18}H_5F_{20}N_3O$ requires C, 33.8; H, 0.76; N, 6.37%).

Synthesis of 14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene (45).

A mixture of 1,1-dimethyl-1-silaethoxy-1,1-dimethyl-1-silaethane (0.6 g, 2.9 mmol), dried CsF (0.7 g, 4.6 mmol) and {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine **(44)** (3 g, 8 mmol), in anhydrous monoglyme (150 ml) was heated to 85 °C under an atmosphere of dry nitrogen. The

mixture was heated over 5 d before being allowed to cool to room temperature and water (20 ml) added. Extraction into DCM (2-x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 5:1) gave a yellow solid, which after recrystallisation from methanol three times gave *14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene* **(45)** (0.27 g, 15%,) as a white solid, mp 155 – 159 °C; (Found C, 35.5; H, 1.26; N, 6.20; $C_{20}H_9F_{18}N_3O_3$ requires C, 35.3; H, 1.37; N, 6.17%).

Synthesis of 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine (46).

A mixture containing sodium hydride (0.76 g, 20 mmol), BINAP (2.5 g, 9.0 mmol), perfluoro-4-isopropylpyridine **(1)** (6 g, 19 mmol) in monoglyme (60 ml) was heated under reflux under an atmosphere of dry nitrogen over 10 h. After cooling, water (10 ml) was added dropwise. Extraction into DCM (3 x 30 ml) enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent removed on a rotary evaporator. Column chromatography (hexane/ether, 4:1) followed by recrystallisation twice from methanol gave *3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine* as a white solid **(46)** (6.4 g, 80%); mp >250 °C; (Found C, 48.8; H, 1.31; N, 3.20 $C_{36}H_{12}F_{20}N_2O_2$ requires C, 48.9; H, 1.37; N, 3.17%).

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane (47).

A mixture containing sodium hydride (2.0 g, 54 mmol) and 1H,1H,2H,2H-perfluorooctan-1-ol (20 g, 54 mmol) in THF (30 ml) was stirred at room temperature over 30 minutes before being transferred dropwise to a solution of pentafluoropyridine (10 g, 60 mmol) in THF (20 ml) at -40 ° under an atmosphere of dry nitrogen. The mixture was stirred over 4 hours before warming to room temperature and water (10 ml) added. Extraction into DCM (2 x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Distillation under reduced pressure gave *3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane* as a colourless liquid **(47)** (41%, 11 g); bp 80

°C at 0.1 mbar; (Found C, 30.6; H, 0.80; N, 2.70; $C_{13}H_4F_{17}NO$ requires C, 30.4; H, 0.79; N, 2.73%).

Synthesis of methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine (48).

A mixture containing N,N`-dimethyl-1,2-diaminoethane (0.5 g, 7.5 mmol) and *3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane* (47) (6 g, 12 mmol) in THF (30 ml) was heated to 70 °C over 2 days before being cooled and a saturated solution of aqueous sodium hydrogen carbonate (30 ml) added. Extraction into perfluoromethylcyclohexane (2-x 50 ml) enabled recovery of products. The combined organic phases were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Recrystallisation from petroleum ether 40-60, gave *methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine* **(48)** as a white solid **(48)** (5.9 g, 76%), mp 54-57°C; (Found, C, 33.4; H, 1.62; N, 5.15; $C_{30}H_{18}F_{32}N_4O_2$ requires C, 33.5; H, 1.68; N, 5.20%).

Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16yloxy]octane (49).

A mixture containing N,N`-dimethyl-1,2-diaminoethane (0.13 g, 1.5 mmol) and methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine **(48)** (4 g, 3.7 mmol) in THF (30 ml) was heated to 170 °C over 7 days before being cooled and a saturated solution of aqueous sodium hydrogen carbonate (30 ml) added. Continuous extraction over 10 hours, into perfluoromethylcyclohexane enabled recovery of products. The solvent was removed on a rotary evaporator. Recrystallisation from petroleum ether 40-60 and acetone (10:1) gave *3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16yloxy]octane* **(49)** as colourless needles (0.4 g, 26%); mp 160-162 °C; (Found C, 36.1; H, 2.57; N, 7.46; $C_{34}H_{28}F_{30}N_6O_2$ requires C, 36.4; H, 2.51; N, 7.49%).

Metal Picrate Extraction Studies.

Aqueous solutions containing picric acid (5.0 mM) and the alkali metal fluoride (50.0 mM) were prepared. Into a capped vial was placed 1.0 ml of the metal picrate solution and 1.0 ml of the macrocycle (5.0 mM) in DCM. The resulting two-phase system was then mixed together for 30 minutes using a mechanical shaker. The samples were then allowed to stand for 1 hour before a sample (10 μl) of the aqueous phase was then removed and made up to a 5.0 ml sample using acetonitrile. The absorption spectrum of the solution was then measured, in a 1.0 cm silica-cell, using a UV2 UV/VIS spectrometer at 275 nm. This was referenced to a blank solution containing DCM and the metal picrate under investigation to account for any slight solubility of the metal picrate in DCM.

4) Experimental to Chapter IV.

Synthesis of 2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (51) and 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine (50).

Under an atmosphere of dry nitrogen an autoclave (250 ml) was charged with TDAE (0.5 g, 2.5 mmol) and tetrafluoropyrimidine (30 g, 200 mmol). The autoclave was sealed and hexafluoropropene (60 g, 400 mmol) was transferred into the autoclave under vacuum. The autoclave was then heated to 60 °C over 20 hours before being cooled and opened to vacuum; no gases were recovered. The autoclave contents were transferred to a RB flask and transferred under vacuum to separate the products from the unwanted non-volatile components. Distillation at atmospheric pressure gave *2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine* **(51)** as a colourless liquid (8 g, 10%); bp 118 °C; (Found C, 27.8; N, 9.3; $C_7F_{10}N_2$ requires C, 27.7; N, 9.3%) and *4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine* **(50)** as a colourless liquid (45 g, 60%); bp 148-149 °C; (Found M^+ 451.979989; $C_{10}F_{16}N_2$ requires M^+ 451.979989).

Synthesis of 2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (52).

A mixture containing perfluoro-4-isopropylpyrimidine **(51)** (2.0 g, 6.6 mmol), sodium methoxide (0.4 g, 7.0 mmol) and THF (20 ml) was heated under reflux over 20 hours before being cooled and water (10 ml) added. Extraction using DCM (2 x 15 ml) enabled recovery of products. The organic phase was dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 10:1)

gave *2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine* **(52)** as a colourless liquid (1.1 g, 58%); bp 179-180 °C.

Synthesis of 5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (53).

A mixture containing perfluoro-4-isopropylpyrimidine **(51)** (3.0 g, 9.8 mmol) and sodium methoxide (1.1 g, 30 mmol) in THF (20 ml) was heated under reflux over 20 hours before being cooled and water (10 ml) added. Extraction using DCM (2-x 15 ml) enabled recovery of organic components. The combined organic layers were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Column chromatography on silica gel (hexane/ethyl acetate 10:1) gave *5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine* **(53)** as a colourless liquid(0.86 g, 20%); bp 210 – 212 °C.

Synthesis of 6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (54).

A mixture containing perfluoro-4-isopropylpyrimidine (51) (5.0 g, 17 mmol), CsF (1.3 g, 8.5 mmol) in monoglyme (60 ml) were stirred in a round bottom flask under an atmosphere of dry nitrogen. 1-[2-(1,1-dimethyl-1-silaethoxy]-1,1-dimethyl-1-silaethane (1.4 g, 6.8 mmol) was added to the solution slowly using a syringe and the mixture heated under reflux over 10 hours before being cooled and water (10 ml) added. Extraction into DCM (2 x 30 ml) enabled recovery of organic components. The combined organic phases were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 1:1) gave *6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine* **(54)** as a colourless liquid (1.1 g, 20%); bp 277-279 °C; Rf, 0.60; (Found, C, 30.6; H, 0.80; N, 8.95; $C_{16}H_4F_{18}N_4O_2$ requires, C, 30.7; H, 0.64; N, 8.95%).

Synthesis of 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine (55).

A mixture containing 4,6-bisperfluoroisopropylpyrimidine **(50)** (3.0 g, 9.8 mmol) and sodium methoxide (1.4 g, 20 mmol) in diglyme (20 ml) was heated to 180 °C over 20 hours before being cooled and water (10 ml) added. Continuous extraction into perfluoromethylcyclohexane enabled recovery of products. The solvent was removed on a rotary evaporator giving the crude product as a white solid. Recrystallisation from

hexane twice gave *4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine* **(55)** as a white solid (2.2 g, 71 %); mp 68 – 71 °C; (Found, C, 28.3; H, 0.38; N, 6.05%; $C_{11}H_3F_{15}N_2O$ requires, C, 28.5; H, 0.65; N, 6.04%).

Synthesis of 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine (56).

4,6-bisperfluoroisopropylpyrimidine **(50)** (3 g, 6.6 mmol) was added dropwise to a mixture of sodium hydride (0.2 g, 8 mmol) and dodecanol (1.3 g, 6.6 mmol) and the mixture was heated under reflux over 3 days before being cooled and water (20 ml) added slowly. Extraction into perfluoromethylcyclohexane (2 x 40 ml) enabled recovery of crude products. Column chromatography (hexane) gave *4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine* **(56)** as a white solid (2.4 g, 59%); mp 88-90 °C; (Found, C, 42.7; H, 4.08; N,4.53; $C_{22}H_{25}F_{15}N_2O$ requires, C, 42.7; H, 4.03; N, 4.58%).

Synthesis of 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine (57).

A mixture containing 4,6-bisisopropylpyrimidine **(50)** (4.0 g, 8.8 mmol), 1-[2-(1,1-dimethyl-1-silaethoxy]-1,1-dimethyl-1-silaethane (0.7 g, 3.4 mmol), CsF (0.5 g, 3.3 mmol) in diglyme (25 ml) was heated to 85 °C over 6 hours before being cooled and water (10 ml) added. Continuos extraction into perfluoromethylcyclohexane enabled recovery of products. The solvent was removed on a rotary evaporator. Recrystallisation from hexane gave *4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine* **(57)** as a white solid (2.1 g, 70 %); mp 81-83 °C; (Found, C, 28.2; H, 0.39; N, 6.00; $C_{22}H_4F_{30}N_4O_2$ requires, C, 28.5; H, 0.44; N, 6.04%).

Synthesis of {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine (58).

A mixture containing 4,6-bisperfluoroisopropylpyrimidine **(50)** (2.0 g, 6.6 mmol) and diethylamine (1.3 g, 18 mmol) in THF (20 ml) was heated to 70 °C over 20 hours before being cooled and water (10 ml) added. Extraction using DCM (2-x 20 ml) enabled recovery of organic products. The combined organic layers were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *{4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-*

yl}diethylamine **(58)** as a white solid (1.2 g, 55%); mp 45-48 °C; Rf, 0.32; (Found, C, 33.0; H, 1.94; N, 8.35; $C_{14}H_{10}F_{15}N_3$ requires, C, 33.3; H, 8.32; H, 1.99%).

Synthesis of {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine (59).

A mixture containing 4,6-bisperfluoroisopropylpyrimidine **(50)** (3.0 g, 9.8 mmol) and benzylamine (2.8 g, 26 mmol) in THF (20 ml) was heated to 70 °C over 20 hours before being cooled and water (10 ml) added. Extraction using DCM (2-x 20 ml) enabled recovery of organic products. The combined organic layers were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *{4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine* **(59)** as a white solid (3.0 g, 85%); Rf, 0.29; mp, 50-53 °C; (Found, C, 37.9; H, 1.51; N, 7.77; $C_{17}H_8F_{15}N_3$ requires; C, 37.9; H, 1.50; N, 7.79%).

Synthesis of 2,5,6-trifluoro-4-methoxypyrimidine (60).

A solution of sodium methoxide (2.8 g, 50 mmol) in methanol (50 ml) was added to a solution of tetrafluoropyrimidine (10 g, 65 mmol) in methanol (10 ml) via a syringe pump over 6 hours at 0 °C. The mixture was allowed to reach room temperature before water (10 ml) was added. Extraction using DCM (2 x 30 ml) enabled recovery of organic products. The combined organic phases were dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Reduced pressure distillation of the crude product mixture gave *2,5,6-trifluoro-4-methoxypyrimidine* **(60)** (6.0 g, 56%) as a colourless liquid; bp 65 °C at 40 mbar; Found (C, 36.5; H, 1.91; N, 17.0; $C_5H_3F_3N_2O$, requires, C, 36.6, H; 1.84, N; 17.1%).

Synthesis of 6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine (62).

1-[2-(1,1-dimethyl-1-silaethoxy]-1,1-dimethyl-1-silaethane (2.5 g, 12 mmol) was added slowly to a solution of 2,5,6-trifluoro-4-methoxypyrimidine **(60)** (5 g, 30 mmol) and CsF (2.7 g, 17 mmol) in monoglyme (60 ml) under an atmosphere of dry nitrogen. The mixture was heated to 75 °C over 20 hours before being cooled and the reaction solvent was removed on a rotary evaporator and water (10 ml) added. Extraction using DCM (2 x 20ml) enabled recovary of organic products. The combined organic phases were dried ($MgSO_4$) before the solvent was removed on a rotary evaporator. Recrystallisation 3 times from acetone gave *6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-*

difluoro-4-methoxypyrimidine **(62)** as a white solid (0.6 g, 14%); mp 150 – 152 °C; (Found, C, 41.1; H, 2.87; N, 15.8; $C_{12}H_{10}F_4N_4O_4$, requires, C, 41.2; H, 2.88; N, 16.0%).

Synthesis of 4,6-bis(tert-butoxy)-2,5-difluoropyrimidine (63).

A solution of potassium tertiary butoxide (7.5 g, 66 mmol) in THF (60 ml) was added to a solution of tetrafluoropyrimidine (10 g, 66 mmol) over 6 hours under an atmosphere of dry nitrogen. The reaction vessel was kept in an ice bath at 0 °C and after 6 hours was allowed to warm to room temperature and the solvent was removed on a rotary evaporator. The crude material was washed through a filter with hot acetone and DCM (4 x 25 ml) and the solvents removed on a rotary evaporator. The crude solid was recrystallised 3 times from hexane 10, acetone 1 solution to give *4,6-bis(tert-butoxy)-2,5-difluoropyrimidine* **(63)** as a white solid (10.1 g, 74%); mp 89-91 °C; (Found, C, 55.4; H, 7.07; N, 10.7; $C_{12}H_{18}F_2N_2O_2$ requires C, 55.4; H, 7.07; N, 10.8%).

5) Experimental to Chapter V.

Reaction of Pentafluoropyridine with Trifluoromethyltrimethylsilane – General Procedure.

A mixture of pentafluoropyridine (2 g, 12 mmol), anhydrous fluoride ion source (0.12 mmol) in the required solvent (50 ml) was heated to the required temperature under an atmosphere of dry nitrogen. Trifluoromethyltrimethylsilane was added via syringe (2.3 g, 15 mmol) and the solution stirred for the required time. ^{19}F NMR spectroscopy was used to determine the rate of conversion to the trifluoromethylated products **(64)**.

Reaction in DMF at 50 °C gave 62% conversion to *2,3,5,6-tetrafluoro-4-trifluoromethylpyridine* **(64)** which was obtained by direct distillation from the solvent as a colourless liquid (0.2 g, 10%); bp 85 °C; (Found C, 32.7; N, 6.40; $C_6F_7N_1$ requires C, 32.9; N, 4.60%).

Synthesis of 2,3,5-trifluoro-6-phenoxy-4-(trifluoromethyl)pyridine (65)

To a stirred solution of phenol (0.07 g, 0.9 mmol) in THF (20 ml) was added sodium metal (0.02 g, 0.9 mmol) and the solution was heated under reflux over 1 hour to enable hydrogen evolution before 2,3,5,6-tetrafluoro-4-trifluoromethylpyridine **(64)** (0.2 g, 0.9 mmol) was added dropwise. The mixture was than heated to 75 °C over 6 hours before being cooled and water (10 ml) was added dropwise slowly, before extraction into DCM (2 x 30 ml) enabled recovery of organic products. Column chromatography on silica gel (hexane) gave *2,3,5-trifluoro-6-phenoxy-4-(trifluoromethyl)pyridine* **(65)** as a white solid

(0.2 g, 77%); mp 51-52 °C; Rf 0.32; (Found C, 49.0; H, 1.63; N, 4.69; $C_{12}H_{10}F_6NO$ requires C, 49.1; H, 1.70; N, 4.70%).

Synthesis of 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine (66).

A stainless steel autoclave was charged with pentafluoropyridine (20 g, 120 mmol), dried CsF (1.0 g 6.6 mmol) and anhydrous tetraglyme (25 ml) under an atmosphere of dry nitrogen. The autoclave was sealed and octafluorobut-2-ene (20 g, 100 mmol) was transferred into the autoclave under vacuum. The autoclave was heated to 60 °C over 3 days before being cooled and opened to vacuum; no gases were recovered. The autoclave was opened and water (20 ml) was added. Extraction into perfluoromethylcyclohexane (3 x 30 ml) followed removal of solvent on a rotary evaporator enabled recovery of products. Distillation under reduced pressure (10 mbar, bp 60 °C) gave *2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine* **(66)** as a colourless liquid (25 g, 71%); bp 143 °C ; (Found M^+ 368.982178; $C_9F_{13}N_1$ requires M^+ 368.982178).

Synthesis of (1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol (67).

A mixture containing (1R,2S)-ephedrine, (0.94 g, 5.7 mmol) and 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine **(66)** (2.0 g, 5.7 mmol) in THF (20 ml) was heated to 75 °C over 20 hours before the solvent was removed on a rotary evaporator and water (10 ml) was added. Extraction into DCM (2 x 30 ml), enabled recovery of products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane/ethyl acetate 10:1) gave *(1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol* **(67)** as a white solid (1.8 g, 65%); mp 61-62 °C, Rf 0.45; (Found C, 44.1; H, 2.73; N, 5.29; $C_{19}H_{14}F_{12}N_2O$ requires C, 44.3; H, 2.74; N, 5.45%).

Synthesis of 3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile (68) and 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile (69)

A stainless steel autoclave (160 ml) was charged with tetrafluorophthalonitrile (35 g, 0.18 mol), dried CsF (3 g, 0.02 mol) and anhydrous tetraglyme (50 ml) under an atmosphere of dry nitrogen. The autoclave was then sealed and octafluorobut-2-ene (30 g, 0.15 mol) was transferred into the autoclave under vacuum. The autoclave was then heated to 60 °C

over 3 days before being cooled and opened to vacuum; no gases were recovered. The contents of the autoclave were transferred to a separating funnel and water (10 ml) was added. Extraction using perfluoromethylcyclohexane followed by removal of the solvent on a rotary evaporator enabled recovery of crude products. Distillation under reduced pressure (0.1 mbar, bp. 80 °C) gave *3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile* **(68)** as a colourless liquid (8.4 g, 14%); bp 231 °C; (Found M^+ 399.986830 $C_{12}F_{12}N_2$ requires M^+ 399.986830) and (0.1 mbar, bp. 87 °C) *4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile* **(69)** as a colourless liquid (48 g, 53%); bp 245 °C. (Found, C, 31.7; N, 4.40; $C_{16}F_{20}N_2$ requires C, 32.0; N, 4.7).

Synthesis of 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile (70)

A mixture containing phenol (0.3 g, 3.3 mmol) and sodium metal (0.8 g, 3.3 mmol) in THF (25 ml) was heated to reflux over one hour before 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile **(69)** (2 g, 3.3 mmol) was added dropwise. The mixture was heated at 75 °C over 20 hours before being cooled and the solvent removed on a rotary evaporator. The crude product was then transferred to a separating funnel and water (10 ml) added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile* **(70)** (1.04 g, 47%) as a white solid; mp 63-63 °C; Rf 0.39; (Found, C, 39.1; H, 0.68; N, 4.10; $C_{22}H_5F_{19}N_2O$ requires C, 39.2; H, 0.75; N, 4.12%).

Synthesis of 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile (71).

A mixture containing phenol (0.8 g, 8.2 mmol) and sodium metal (0.2 g, 8.2 mmol) in THF (25 ml) was heated to reflux over one hour before 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile **(69)** (2 g, 3.3 mmol) was added dropwise. The mixture was heated at 75 °C over 20 hours before being cooled and the solvent removed on a rotary evaporator. The crude product was then transferred to a separating funnel and water (10 ml) added. Extraction in DCM (2 x 15 ml) enabled recovery of organic products. The organic phase was dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. Column chromatography (hexane) gave *4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-*

dicarbonitrile (71) (0.82 g, 37%) as a white solid; mp 67-68 °C (Found, M^+ 748.045732; $C_{28}H_{10}F_{18}N_2O_2$ requires M^+ 748.045732).

Synthesis of 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile (72).

A mixture containing tetrafluorophthalonitrile (5.0 g, 25 mmol) and dried potassium fluoride (2.2 g, 100 mmol) in anhydrous DMF (25 ml) under an atmosphere of dry nitrogen was heated to 50 °C with a cold-finger condenser attached, containing acteone/CO_2. Trifluoromethyltrimethylsilane (14 g, 100 mmol) in anhydrous DMF (5 ml) was added slowly to the reaction vessel *via* syringe. The mixture was then stirred at 50 °C over 6 hours. The deep red solution was then transferred to an autoclave (160 ml) under an atmosphere of dry nitrogen. Hexafluoropropene (15 g, 90 mmol) was transferred into the autoclave under vacuum. The autoclave was sealed and heated to 85 °C over 48 hours before being opened to vacuum and hexafluoropropene (7.0 g 41 mmol) was recovered. Continuos extraction into perfluoromethylcyclohexane followed by evaporation of the solvent on a rotary evaporator gave the crude product mixture. Column chromatography (hexane) of this mixture gave a very small quantity of *3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile* (72) as a white solid mp 78-79°C; (Found C, 31.6; N, 2.8; $C_{20}F_{17}N_1$ requires C, 31.4; N, 2.8%).

Appendix A NMR Spectroscopy.

Chapter II

1) 3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (3)
2) 3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (4)
3) 2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (5)
4) 2,6-dibutyl-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (6)
5) 6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (7)
6) 2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (8)
7) 4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione (9)
8) 6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (10)
9) 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine (11)
10) 3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine (12)
11) 2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (13)
12) 2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (14)
13) 3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (15)
14) diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine (18)
15) {6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}diethylamine (19)
16) benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine (20)

Chapter III

17) 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene **(35)**

18) 25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene **(37)**

19) 26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene **(39)**

20) 11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20),15,17-hexaene **(42)**

21) 2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene **(43)**

22) 2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol **(44a)**

23) {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine **(44)**

24) 14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene **(45)**

25) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine **(46)**

26) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane **(47)**

27) methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine **(48)**

28) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane (49)

Chapter IV

29) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine (50)

30) 2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (51)

31) 2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (52)

32) 5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (53)

33) 6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (54)

34) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine (55)

35) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine (56)

36) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine (57)

37) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine (58)

38) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine (59)

39) 2,5,6-trifluoro-4-methoxypyrimidine (60)

40) 2,5-difluoro-6-hydroxy-4-methoxypyrimidine (61)

41) 6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine (62)

42) 4,6-bis(tert-butoxy)-2,5-difluoropyrimidine (63)

Chapter V

43) 2,3,5,6-tetrafluoro-4-trifluoromethylpyridine (64)

44) 3,5,6-trifluoro-2-phenoxy-4-trifluoromethylpyridine (65)

45) 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine (66)

46) (1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol **(67)**

47) 3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile **(68)**

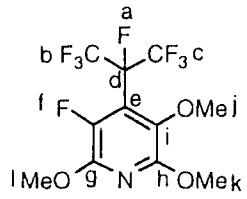
48) 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile **(69)**

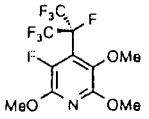
49) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile **(70)**

50) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile **(71)**

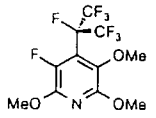
51) 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile **(72)**

1) 3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**3**)





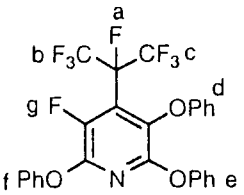
A



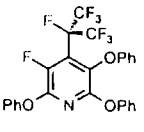
B

Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.76	3	s		j
3.90	6	s		l, k
^{19}F				
-74.9	3	m		b, c of B
-75.1	3	m		b, c of A
-146.3	0.5	br s		f of A
-149.7	0.5	d	$^{4}J_{FF}$ 94.0	f of B
-177.5	0.5	d	$^{4}J_{FF}$ 94.0	a of B
-182.0	0.5	s		a of A
^{13}C				
53.9		s		l ,k
60.5		s		j of A
61.6		s		j c of B
92.2		dsept	$^{1}J_{CF}$ 218	d
			$^{2}J_{CF}$ 37.4	
119.0		m		e
120.3		qd	$^{1}J_{CF}$ 280	b, c
			$^{2}J_{CF}$ 27.7	
133.3		br s		i
135.4		d	$^{1}J_{CF}$ 264	f of A
139.1		s		f of B
146.8		s		g
150.0		s		h

2) 3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**4**)



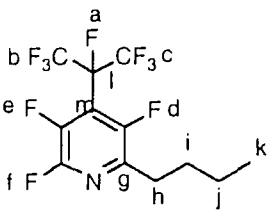
A



B

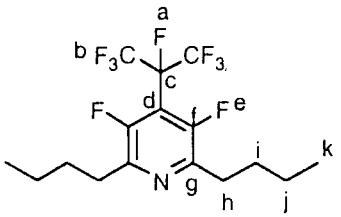
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
6.4 – 7.4		m		d, e, f
^{19}F				
-71.5	3	m		b, c of A
-72.0	3	m		b, c of B
-136.2	0.5	s		g of A
-138.7	0.5	d	$^{4}J_{FF}$ 98.5	g of B
-174.5	0.5	d	$^{4}J_{FF}$ 98.5	a of B
-178.3	0.5	s		a of A

3) 2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**5**)



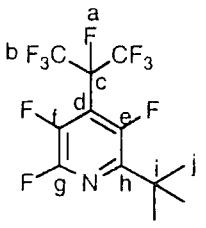
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
0.87	3	t	$^{3}J_{HH}$ 7.6	k
1.30	2	sex	$^{3}J_{HH}$ 7.6	j
1.60	2	quin	$^{3}J_{HH}$ 7.6	i
2.72	2	t	$^{3}J_{HH}$ 7.6	h
^{19}F				
-71.2	6	m		b, c
-82.4	1	s		f
-117.7	1	s		d
-133.7	1	s		e
-175.8	1	br s		a
^{13}C				
14.0		s		k
22.5		s		j
30.4		s		i
31.6		s		h
92.3		dsept	$^{1}J_{CF}$ 214.5 $^{2}J_{CF}$ 35.3	l
119.2		m		m
119.6		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.3	b, c
144 - 149		br overlapping m		e, d, f, g

4) 2,6-dibutyl-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (6)



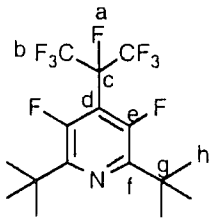
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
0.87	6	t	$^{3}J_{HH}$ 7.6	k
1.30	4	sex	$^{3}J_{HH}$ 7.6	j
1.60	4	quin	$^{3}J_{HH}$ 7.6	i
2.72	4	t	$^{3}J_{HH}$ 7.6	h
^{19}F				
-71.2	6	m		b
-117.7	2	m		e
-175.8	1	m		a
^{13}C				
13.7		s		k
23.3		s		j
30.5		s		h
92.3		dsept	$^{1}J_{CF}$ 215 $^{2}J_{CF}$ 35.3	c
119.2		m		d
144-149		br m		f, g

5) 6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (7)



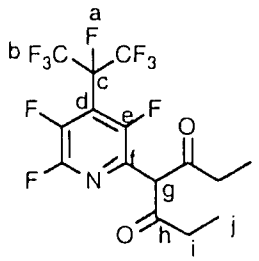
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.38		s		j
^{19}F				
-75.3	6	m		b
-86.4	1	br s		g
-115.0	1	br s		e
-137.3	1	br s		f
-179.5	1	m		a
^{13}C				
28.3		s		j
37.6		s		i
92.3		dsept	$^{1}J_{CF}$ 216	c
			$^{2}J_{CF}$ 35.3	
119.2		m		d
119.6		qd	$^{1}J_{CF}$ 287	b
			$^{2}J_{CF}$ 27.3	
143-148		br m		h, e, g, f

6) 2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (8)



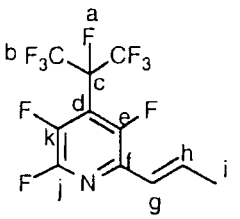
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.41		s		h
^{19}F				
-72.1	6	s		b
-112.0	1	br s		e
-115.2	1	m		e
-175.8	1	m		a
^{13}C				
28.6		s		h
38.2		s		g
92.4		dsept	$^{1}J_{CF}$ 211 $^{2}J_{CF}$ 35.3	c
112.1		m		d
120.4		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.3	b
147-156		br m		e, f

7) 4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione (**9**)



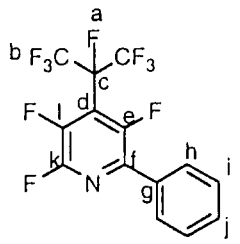
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.23	6	t	$^{3}J_{HH}$ 7.2	j
4.30	4	q	$^{3}J_{HH}$ 7.2	i
4.98	1	s		g
^{19}F				
major rotamer				
-74.6	6	m		b
-85.4	1	br s		k
-119.0	0.5	br s		e
-132.3	0.5	br s		l
-180.3	1	br s		a
minor rotamer				
-74.6	6	m		b
-85.4	1	br s		k
-120.4	0.5	br s		e
-129.2	0.5	br s		l
-180.3	1	br s		a
^{13}C				
13.6		s		j
54.7		s		i
62.6		s		g
91.6		dsept	$^{1}J_{CF}$ 214 $^{2}J_{CF}$ 35.7	c
115.8		m		d
119.8		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 26.9	b
144-154		br m		e, f, l, k
164.9		s		h

8) 6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**10**)



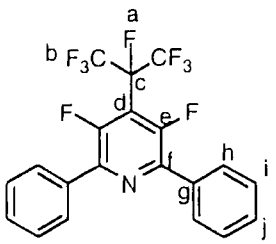
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.91	3	d	$^{3}J_{HH}$ 6.8	i
2.09	3	d	$^{3}J_{HH}$ 8.4	i
6.17	1	m		h
6.42	1	d	$^{3}J_{HH}$ 12.0	g
6.96	1	m		g
^{19}F				
major rotamer				
-75.1	6	m		b
-85.6	0.5	br s		j
-120.4	0.5	br s		e
-136.4	0.5	br s		k
-179.9	1	br s		a
minor rotamer				
-75.1	6	m		b
-86.6	0.5	br s		j
-127.6	0.5	br s		e
133.3	0.5	br s		k
-179.9	1	br s		a
^{13}C				
15.4		s		i
18.7		s		i
117.9		m		d
120.0		qd	$^{1}J_{CF}$ 231 $^{2}J_{CF}$ 29.0	b
128.9		m		h
137.2		t	$^{3}J_{CF}$ 3.8	g
138.1		t	$^{3}J_{CF}$ 2.2	g
144-148		br m		e, j, k, f

9) 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine (**11**)



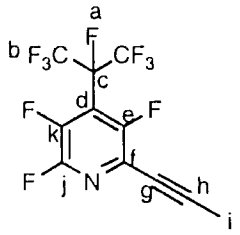
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
7.41-7.90		m		h, i, j
^{19}F				
major rotamer				
-75.2	6	m		b
-84.8	0.5	br s		k
-120.0	0.5	br s		e
-134.7	0.5	d	$^{4}J_{FF}$ 81.2	l
-179.5	0.5	d	$^{4}J_{FF}$ 81.2	a
minor rotamer				
-75.2	6	m		b
-86.0	0.5	br s		k
-122.1	0.5	br s		e
-131.7	0.5	br s		l
-180.3	0.5	br s		a
^{13}C				
91.9		dsept	$^{1}J_{CF}$ 214 $^{2}J_{CF}$ 37.2	c
119.5		m		d
119.9		qd	$^{1}J_{CF}$ 294 $^{2}J_{CF}$ 27.2	b
128.9		s		h
129.2		s		i or j
129.9		s		i or j
130.1		s		g
143-155		br m		e, f, l, k

10) 3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine (**12**)



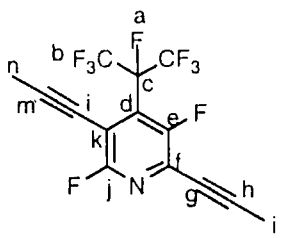
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
7.41-7.90		m		h, i and j
^{19}F				
major rotamer				
-75.2	3	m		b
-117.7	1	br s		e
-179.2	1	m		a
minor rotamer				
-75.2	3	m		b
-120.6	1	m		e
-179.2	1	m		a
^{13}C				
92.4		dsept	$^{1}J_{CF}$ 213 $^{2}J_{CF}$ 35.3	c
113.2		dt	$^{2}J_{CF}$ 21.6 $^{2}J_{CF}$ 12.9	d
120.4		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.3	b
128.9		s		i
129.2		s		j or k
129.9		s		j or k
130.1		s		h
143-155		br m		e, g

11) 2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(13)**



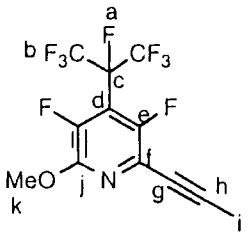
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.10		s		i
^{19}F				
major rotamer				
-73.7	6	m		b
-83.0	0.5	br s		j
-113.3	0.5	br s		e
-131.1	0.5	br s		k
-178.7	1	br s		a
minor rotamer				
-73.7	6	m		b
-83.9	0.5	br s		j
-115.5	0.5	br s		e
-128.1	0.5	br s		k
-178.7	1	br s		a
^{13}C				
4.64		s		i
71.2		s		h
92.0		dsept	$^{1}J_{CF}$ 216	c
			$^{2}J_{CF}$ 35.2	
97.0		s		g
116.1		m		d
119.8		qd	$^{1}J_{CF}$ 287	b
			$^{2}J_{CF}$ 27.0	
133.0		m		f
147.9		dm	$^{1}J_{CF}$ 219	e or k or j
148.0		dm	$^{1}J_{CF}$ 250	e or k or j
154.0		dm	$^{1}J_{CF}$ 275	e or k or j

12) 2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**14**)



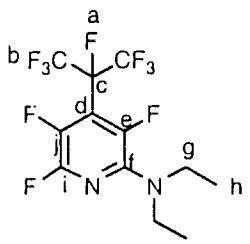
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.10		s		i, n
^{19}F				
-62.3	1	s		j
-73.0	6	s		b
-117.8	1	s		e
-174.3	1	s		a
^{13}C				
5.07		s		i, n
68.8		s		m
72.2		s		h
92.5		dsept	$^{1}J_{CF}$ 214 $^{2}J_{CF}$ 27.0	c
98.2		s		g
102.3		s		l
116.1		m		d
119.8		qd	$^{1}J_{CF}$ 260 $^{2}J_{CF}$ 27.0	b
127.3		m		k or f
128.6		m		k or f
154.0		d	$^{1}J_{CF}$ 260	e or j
159.0		d	$^{1}J_{CF}$ 275	e or j

13) 3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine (**15**)



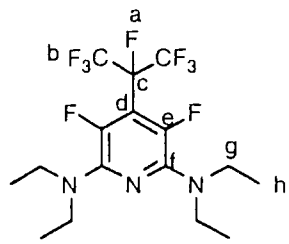
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.1	3	s		i
3.97	3	s		k
^{19}F				
major rotamer				
-75.5	6	m		b
-124.2	0.5	br s		e
-131.4	0.5	br s		l
-180.0	1	br m		a
minor rotamer	1			
-75.5	6	m		b
-126.5	0.5	br s		e
-128.2	0.5	br s		l
-180.0	1	br m		a
^{13}C				
4.65		s		i
54.7		s		k
72.3		s		h
91.8		dsept	$^{1}J_{CF}$ 214 $^{2}J_{CF}$ 27.0	c
94.8		dm	$^{3}J_{CF}$ 6.8	g
113.5		m		d
120.0		qd	$^{1}J_{CF}$ 281 $^{2}J_{CF}$ 25.4	b
150-152		br m		e, f, j, l

14) diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine (**18**)



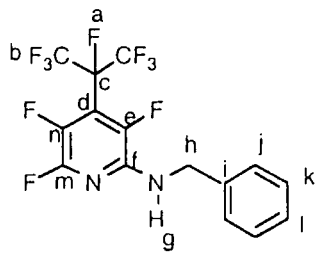
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.30	6	t	$^{3}J_{HH}$ 6.8	h
3.39	4	q	$^{3}J_{HH}$ 6.8	g
^{19}F				
major rotamer				
-75.6	3	m		b
-86.5	0.5	br s		i
-129.0	0.5	br s		e
-154.1	0.5	d	$^{4}J_{FF}$ 89.9	j
-176.4	0.5	d	$^{4}J_{FF}$ 89.9	a
minor rotamer				
-72.5	3	m		b
-87.6	0.5	br s		i
-131.3	0.5	d	$^{4}J_{FF}$ 88.4	e
-150.5	0.5	s		j
-177.3	0.5	d	$^{4}J_{FF}$ 88.4	a
^{13}C				
13.4		s		h
44.6		s		g
92.4		dsept	$^{1}J_{CF}$ 212 $^{2}J_{CF}$ 38.3	c
115.8		m		d
120.2		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.0	b
132-146		br m		e, f, i, j

15) {6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}diethylamine **(19)**



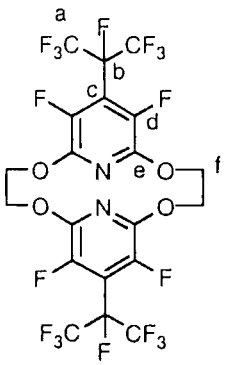
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.71	12	t	$^{3}J_{HH}$ 6.8	h
3.39	8	q	$^{3}J_{HH}$ 6.8	g
^{19}F				
-75.4	6	s		b
-143.5	2	br s		e
-146.9	2	d	$^{4}J_{FF}$ 99.8	e
-179.1	1	d	$^{4}J_{FF}$ 99.8	a
^{13}C				
13.7		s		
44.2		s		
93.0		dsept	$^{1}J_{CF}$ 210	
			$^{2}J_{CF}$ 35.3	
115.8		m		
120.1		qd	$^{1}J_{CF}$ 287	
			$^{2}J_{CF}$ 27.0	
132-146		br m		

16) benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine (**20**)



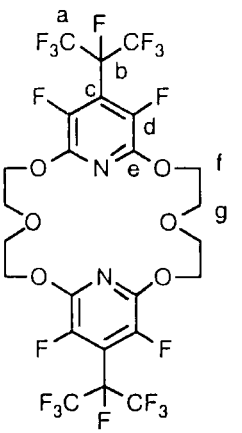
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.62	2	d	$^{3}J_{HH}$ 5.6	h
5.12	1	br s		g
7.32-7.39	5	m		i, j, k
^{19}F				
major rotamer				
-70.8	6	m		b
-87.2	0.5	br s		m
-133.9	0.5	br s		e
-150.1	0.5	br s		n
-175.6	1	br s		a
minor rotamer				
-70.8	6	m		b
86.1	0.5	br s		m
-136.6	0.5	br s		e
-153.3	0.5	br s		n
-175.6	1	br s		a
^{13}C				
45.3		s		h
92.0		dsept	$^{1}J_{CF}$ 212 $^{2}J_{CF}$ 35.5	c
114.6		dddd	$^{2}J_{CF}$ 11.0, 11.0, 10.6 $^{3}J_{CF}$ 3.0	d
120.2		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.3	b
128.1		s		l
128.2		s		j or k
129.1		s		j or k
137.9		s		i
142.0-147.1		br m		e, f, m, n

17) 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene (**35**)



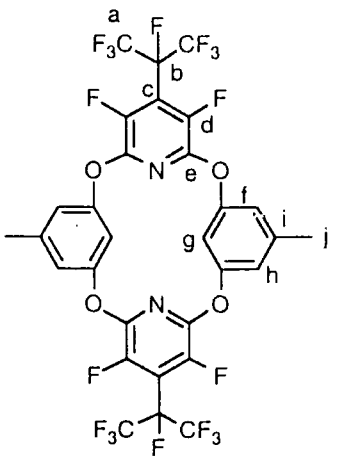
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
20 °C				
5.2-6.8		br s		f
90 °C				
4.70		s		f
^{19}F				
-77.0	12	s		a
-145.1	2	br s		d
-147.9	2	br s		d
-181.7	2	m		b
^{13}C				
65.1		br s		f
93.3		dm	$^{1}J_{CF}$ 212	b
117.1		m		c
121.5		qd	$^{1}J_{CF}$ 288	a
			$^{2}J_{CF}$ 26.6	
127.8		d	$^{1}J_{CF}$ 154	d
130.4		d	$^{2}J_{CF}$ 84.0	e

18) 25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene (**37**).



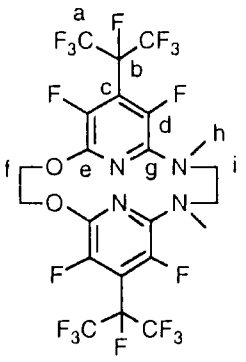
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.88	8	m		f
4.65	8	m		g
^{19}F				
-76.4	12	m		a
-147.1	2	br s		d
-150.0	2	br s		d
-180.7	2	m		b
^{13}C				
66.9	s			f or g
69.9	s			f or g
92.9	dsept	$^{1}J_{CF}$ 211		b
		$^{2}J_{CF}$ 35.3		
114.5	m			c
121.5	qd	$^{1}J_{CF}$ 286		a
		$^{2}J_{CF}$ 27.0		
147.2	br s			e

19) 26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene (**39**).



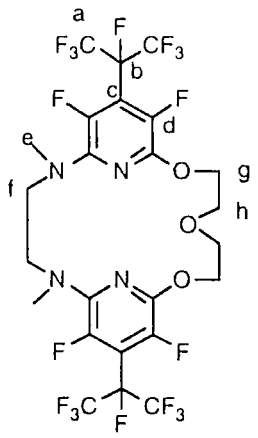
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.33	6	s		j
6.58	2	s		g
6.81	4	s		h
^{19}F				
-75.5	12	m		a
-141.3	2	br s		d
-144.1	2	br s		d
-180.3	2	m		b
^{13}C				
21.1		s		j
112.3		s		i
119.6		s		h
140.9		s		g
152.4		s		f

20) 11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20),15,17-hexaene (**42**).



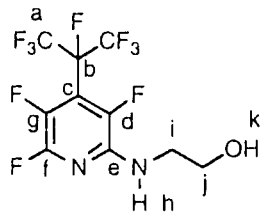
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
20 °C				
3.25		m		h
3.40-5.40		br s		f, i
90 °C				
3.29	6	m		h
3.75	4	br s		i
4.73	4	br s		f
^{19}F				
-74.8	12	m		a
-139.5	2	m		d
-150.6	2	m		d
-178.6	2	m		b
^{13}C				
38.5		s		h
49.0		s		i
62.4		s		f
115.3		m		c
120.7		qd	$^{1}J_{CF}$ 288 $^{2}J_{CF}$ 28.0	a
133.5		m		e or g
136.1		m		e or g
144.5		dm	$^{1}J_{CF}$ 272	d

21) 2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene (**43**)



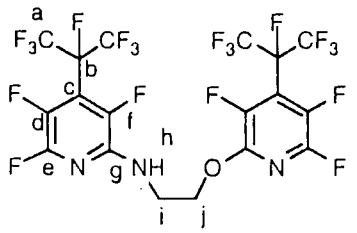
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.74	6	m		e
2.95-3.05	8	m		f, g
3.34	4	m		h
^{19}F				
-74.3	12	m		a
-133.3	4	br s		d
-182.9	2	m		b
^{13}C				
37.3		s		e
43.5		s		f
46.6		s		g or h
47.6		s		g or h
121.1		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 28.1	b

22) 2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol (**44a**).



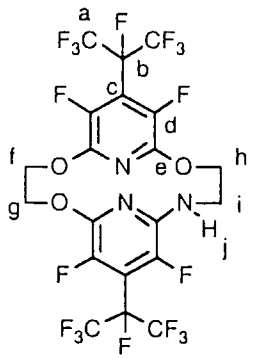
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.69	1	br s		k
3.63	2	m		i or j
3.81	2	m		i or j
5.40	1	br s		h
^{19}F				
-75.8	6	m		a
-92.2	1	m		f
-139.9	1	m		d
-155.3	1	m		g
-180.5	1	m		b
^{13}C				
43.5		s		i
61.4		s		j
92.0		dsept	$^{1}J_{CF}$ 210 $^{2}J_{CF}$ 34.4	b
114.5		m		c
119.8		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 27.0	a
132.1		dm	$^{1}J_{CF}$ 262	d or g
143.1		m		e
147.0		dd	$^{1}J_{CF}$ 234 $^{2}J_{CF}$ 15.5	f

23) {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine (**44**).



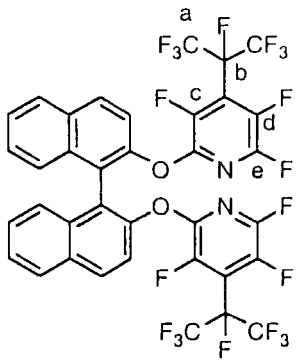
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.83-3.94	2	m		i
4.48-4.62	2	m		j
5.00-5.25	1	m		h
^{19}F				
-75.9	12	m		a
-85.5	2	m		e
-160.0	2	m		d
-163.1	2	m		f
-180.2	2	br s		b
^{13}C				
40.6		s		i
67.2		s		j
92.5		dsept	$^{1}J_{CF}$ 213 $^{2}J_{CF}$ 38.7	b
120.3		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 27.0	a
115.1-117.5		m		c

24) 14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene (45)



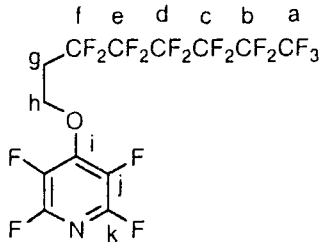
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.78	2			i
4.53-4.84	7			f, g, h, j
^{19}F				
-75.0	12	m		a
-144.7	2	m		d
-147.9	2	m		d
-179.2	2	m		b
^{13}C				
39.5		s		i
62.1		s		f or g or h
62.8		s		f or g or h
64.2		s		f or g or h
92.1		dsept	$^{1}J_{CF}$ 210 $^{2}J_{CF}$ 37.5	b
120.6		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 27.1	a
113.8-115.7		m		c

25) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine (**46**).



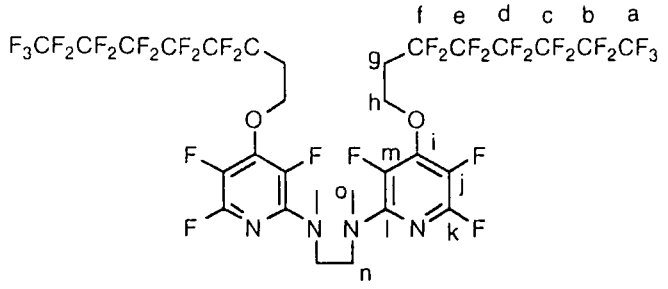
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
7.17-8.17		m		BINAP
^{19}F				
-76.3	12	m		a
-92.8	2	m		e
-135.5	2	m		c
-156.7	2	m		d
-180.9	2	m		b
^{13}C				
121.8-133.7		m		BINAP

26) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane (**47**).



Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.69	2	tt	$^{3}J_{HH}$ 6.4 $^{3}J_{HF}$ 18	g
4.79			$^{3}J_{HH}$ 6.4	h
^{19}F				
-81.6	3	s		a
-90.6	2	s		k
-114.1	2	s		b to f
-122.5	2	s		b to f
-123.6	2	s		b to f
-124.2	2	s		b to f
-126.9	2	s		b to f
-159.5	2	s		j
^{13}C				
31.8		t	$^{2}J_{CF}$ 21.6	g
61.4		s		h
105-122		m		b to f
135.3		dm	$^{1}J_{CF}$ 275	j
144.4		dm	$^{1}J_{CF}$ 241	k
146.5		m		i

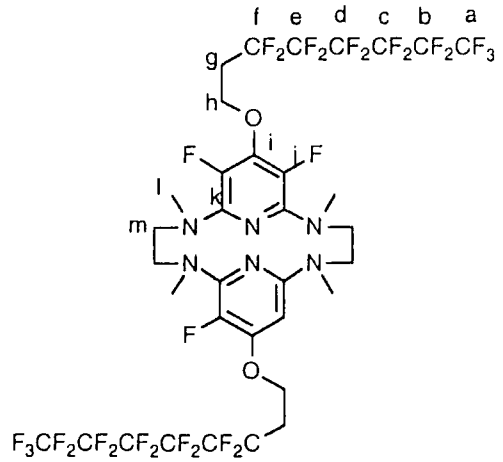
27) methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine (**48**).



Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.61	4	m		g
3.04	6	s		o
3.62	4	s		n
4.58	4	t	$^{3}J_{HH}$ 6.4	h
^{19}F				
-81.3	6	s		a
-90.6	2	m		l
-113.8	4	s		b to f
-122.3	4	s		b to f
-123.6	4	s		b to f
-124.0	4	s		b to f
-126.6	4	s		b to f
-154.2	2	s		m
-170.8	2	s		j
^{13}C				
31.8		t		g
38.2		s		n or o
49.6		s		n or o
65.9		s		h
105-122		m		a to f
129.5		dd	$^{1}J_{CF}$ 249	m
			$^{2}J_{CF}$ 33.0	

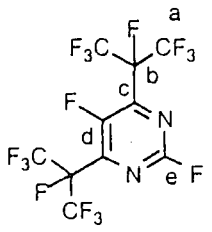
136.9	dd	$^{1}J_{CF}$ 249 $^{3}J_{CF}$ 5.3	j
144.6	dd	$^{1}J_{CF}$ 229 $^{2}J_{CF}$ 13.3	k
141.8	m		l or i
144.6	m		l or i

28) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane (**49**)



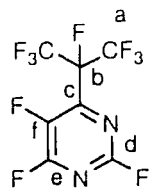
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
2.66	4	m		g
3.16	12	s		l
3.61	8	br s		m
4.46	4	t	$^{3}J_{HH}$ 6.8	h
^{19}F				
-81.2	6	s		a
-113.7	4	s		b to f
-122.3	4	s		b to f
-123.3	4	s		b to f
-123.9	4	s		b to f
-126.5	4	s		b to f
163.5	4	s		j
^{13}C				
31.6		s		g
37.7		s		m
48.2		s		l
65.6		s		h

29) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine (**50**).



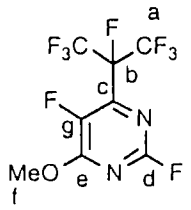
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-48.3	1	m		e
-75.2	12	m		a
-134.5	1	br s		d
-186.5	1	m		b
^{13}C				
91.4		dseptd	$^{1}J_{CF}$ 211 $^{2}J_{CF}$ 33.3 $^{3}J_{CF}$ 3.8	b
119.8		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 26.6	a
148.4		m		c
155.3		dd	$^{1}J_{CF}$ 282 $^{4}J_{CF}$ 6.8	d
155.7		dm	$^{1}J_{CF}$ 223	e

30) 2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (**51**)



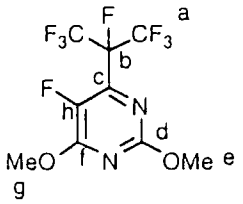
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-48.3	1	d	$^{4}J_{FF}$ 20	d
-70.7	1	s		e
-75.7	6	m		a
-152.6	1	s		f
-187.0	1	m		b
^{13}C				
91.2		dseptm	$^{1}J_{CF}$ 209 $^{2}J_{CF}$ 33.4	b
120.5		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 26.1	a
144.3		m		c
144.3		ddd	$^{1}J_{CF}$ 275 $^{3}J_{CF}$ 9.7 $^{3}J_{CF}$ 8.4	e
154.6			$^{1}J_{CF}$ 223 $^{2}J_{CF}$ 17.5	f
162.4		dm	$^{1}J_{CF}$ 260	d

31) 2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (**52**).



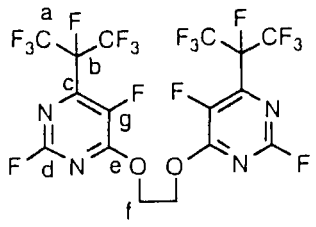
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.17		s		f
^{19}F				
-46.2	1	m		d
-74.6	6	m		a
-151.4	1	m		g
-186.0	1	m		b
^{13}C				
56.4		s		f
119.8		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 27.3	a
144.7		dd	$^{1}J_{CF}$ 275 $^{3}J_{CF}$ 7.6	g
155.0		dm	$^{1}J_{CF}$ 223	d
163.7		m		e

32) 5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (**53**)



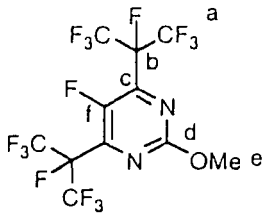
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.96	3	s		e or g
4.10	3	s		e or g
^{19}F				
-74.7	6	m		a
-159.2	1	m		h
-186.2	1	m		b
^{13}C				
55.6		s		e or g
56.0		s		e or g
91.1		dseptd	$^{1}J_{CF}$ 241 $^{2}J_{CF}$ 28.8 $^{3}J_{CF}$ 3.8	b
120.1		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 26.2	a
138.8		m		c
142.6		d	$^{1}J_{CF}$ 270	h
158.8		m		f or d
162.5		m		f or d

33) 6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine (**54**)



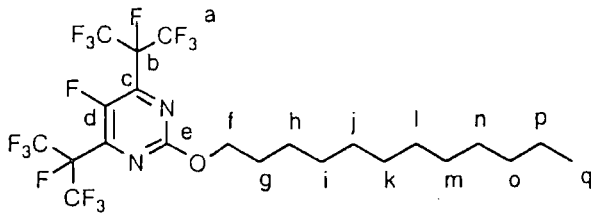
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.79		s		f
^{19}F				
-46.3	2	m		d
-74.7	12	m		a
-150.7	2	m		g
-186.1	2	m		b
^{13}C				
66.4				f
91.0		dseptd	$^{1}J_{CF}$ 213	b
			$^{2}J_{CF}$ 33.4	
			$^{3}J_{CF}$ 3.4	
121.2		qd	$^{1}J_{CF}$ 287	a
			$^{2}J_{CF}$ 28.6	
141.2		m	m	c
144.4		dd	$^{1}J_{CF}$ 275	g
			$^{3}J_{CF}$ 7.9	
154.7		dm	$^{1}J_{CF}$ 223	d
162.9		m		e

34) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine (**55**)



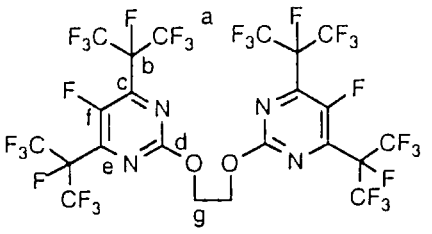
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.97		s		e
^{19}F				
-75.3	12	m		a
-163.1	1	tm	J_{FF} 55.3	f
-185.5	2	dm	J_{FF} 55.3	b
^{13}C				
58.3				e
91.3		dseptd	$^{1}J_{CF}$ 208 $^{2}J_{CF}$ 32.3 $^{3}J_{CF}$ 3.4	b
120.3		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 26.9	a
144.8		d	$^{1}J_{CF}$ 260	f
144.9		dd	$^{2}J_{CF}$ 22.5 $^{2}J_{CF}$ 223	c
163.7		m		d

35) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine (**56**)



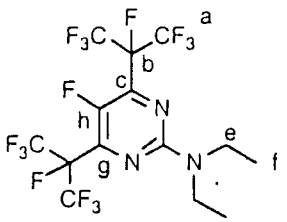
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
0.88	3	m		q
1.27	18	br m		h, i, j, k, l, m, n, o, p
1.84	2	m		g
4.38	2	t	$^{3}J_{HH}$ 6.8	f
^{19}F				
-74.4	12	m		a
-141.9	1	m		d
-185.5	2	m		b
^{13}C				
14.1		s		q
70.6		s		f
91.4		dseptd	$^{1}J_{CF}$ 212 $^{2}J_{CF}$ 33.0 $^{3}J_{CF}$ 3.4	b
120.0		qd	$^{1}J_{CF}$ 280 $^{2}J_{CF}$ 26.6	a
147.3		m		c
151.0		d	$^{1}J_{CF}$ 280	d
159.1		s		e

36) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine (**57**)



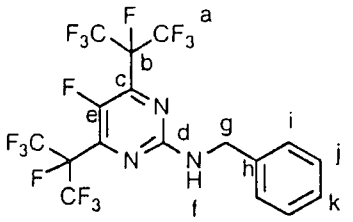
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.79				g
^{19}F				
-74.4	24	m		a
-139.9	2	m		f
-185.6	4	m		b
^{13}C				
91.2		dseptd	$^{1}J_{CF}$ 212 $^{2}J_{CF}$ 33.4 $^{3}J_{CF}$ 3.5	b
119.5		qd	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 26.6	a
147.6		dd	$^{2}J_{CF}$ 8.6 $^{2}J_{CF}$ 10.6	c, e
151.5		d	$^{1}J_{CF}$ 281	f
158.3		m		d

37) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine (**58**)



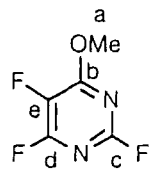
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.17	3	t	$^{3}J_{HH}$ 7.2	f
3.63	2	q	$^{3}J_{HH}$ 7.2	e
^{19}F				
-75.3	12	s		a
-156.5	1	m		h
-186.3	2	m		b
^{13}C				
12.5		q	$^{1}J_{CH}$ 126	e
44.0		tm	$^{1}J_{CH}$ 123	f
91.3		dseptm	$^{1}J_{CF}$ 214 $^{2}J_{CF}$ 34.5 $^{3}J_{CF}$ 3.3	b
120.9		qd	$^{1}J_{CF}$ 286 $^{2}J_{CF}$ 26.0	a
148.1		d	$^{1}J_{CF}$ 269	h
145.7		m		c, g
155.8		m		d

38) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine (**59**).



Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.55	2	d	$^{3}J_{HH}$ 6.0	g
5.84	1	br s		f
7.25-7.39	5	m		i, j, k
^{19}F				
-74.3	12	m		a
-149.2	1	m		e
-185.4	2	m		b
^{13}C				
46.4				g
91.3		dseptm	$^{1}J_{CF}$ 214	b
			$^{2}J_{CF}$ 34.5	
120.3		qd	$^{1}J_{CF}$ 286	a
128.1		s		i
128.2		s		k
129.0		s		j
137.4		s		h
144.8		d	$^{1}J_{CF}$ 270	e
156.2		m		d

39) 2,5,6-trifluoro-4-methoxypyrimidine (**60**)

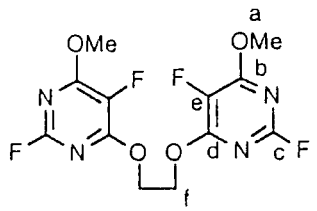


Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
4.14				a
^{19}F				
-49.7	1	s		c
-85.3	1	s		d
-178.5	1	s		e
^{13}C				
56.8		s		a
130.4		dm	$^{1}J_{CF}$ 255	d
153.4		dm	$^{1}J_{CF}$ 217	e
158.3		dm	$^{1}J_{CF}$ 246	c
163.5		m		b

40) 2,5-difluoro-6-hydroxy-4-methoxypyrimidine (**61**)

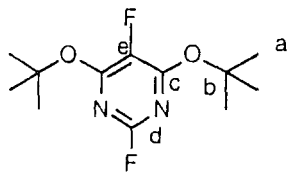
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.87	3	s		a
13.3	1	br s		d
^{19}F				
-91.8	1	s		c
-183.7	1	s		e
^{13}C				
55.9		s		a
128.0		dm	$^{1}J_{CF}$ 237	e
153.1		m		d
155.2		dm	$^{1}J_{CF}$ 243	c
157.6		m		b

41) 6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine (**62**).



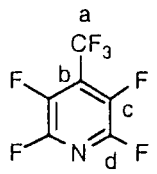
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
3.34		s		a
3.97		s		f
^{19}F				
-48.9	2	s		e
-178.2	2	s		c
^{13}C				
55.6		s		a
66.2		s		f
130.9		dm	$^{1}J_{CF}$ 248	c
153.2		dm	$^{1}J_{CF}$ 212	e
159.4		m		b or d
160.5		m		b or d

42) 4,6-bis(tert-butoxy)-2,5-difluoropyrimidine (**63**).



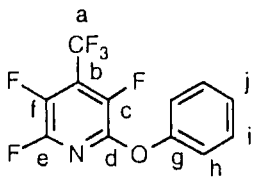
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.61		s		a
^{19}F				
-49.0	1	s		d
-174.8	1	s		e
^{13}C				
28.6		s		a
84.4		s		b
132.3		dm	$^{1}J_{CF}$ 249	e
152.5		dm	$^{1}J_{CF}$ 211	d
159.2		m		c

43) 2,3,5,6-tetrafluoro-4-trifluoromethylpyridine (**64**)



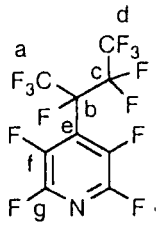
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-66.8	3	m		a
-95.4	2	s		d
-149.0	2	s		c
^{13}C				
119.7		qm	$^{1}J_{CF}$ 220	a
121.8		m		b
139.4		dm	$^{1}J_{CF}$ 217	c
144.4		dm	$^{1}J_{CF}$ 198	d

44) 3,5,6-trifluoro-2-phenoxy-4-trifluoromethylpyridine (**65**)



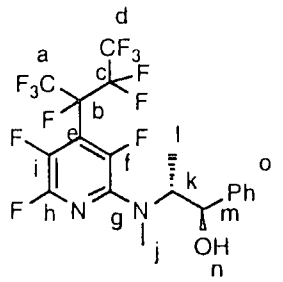
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
6.96 – 7.38				h, i, j
^{19}F				
-58.3	3	t	$^{4}J_{FF}$ 20.3	a
-88.5	1	m		e
-138.8	1	m		f
-147.7	1	m		c
^{13}C				
120.0		qm	$^{1}J_{CF}$ 274	a
126.0		s		j
129.9		s		i
136.3		dd	$^{1}J_{CF}$ 266.3 $^{2}J_{CF}$ 31.8	e
140.8		dd	$^{1}J_{CF}$ 273 $^{3}J_{CF}$ 6.4	c
144.4		ddd	$^{1}J_{CF}$ 241 $^{2}J_{CF}$ 20.0 $^{3}J_{CF}$ 3.8	f
152.2		s		g

45) 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine (**66**).



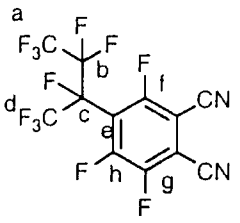
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-73.7	3	s		a
-81.3	3	s		d
-87.4	2	m		g
-88.9	2	m		g
-119.4 and		AB	J_{AB} 293	c
–122.4				
-134.5	2	m		f
-139.2	2	dm	$^{4}J_{FF}$ 97.4	f
-183.3	1	dm	$^{4}J_{FF}$ 95.5	b
^{13}C				
93.9		dsexm	$^{1}J_{CF}$ 212	b
			$^{2}J_{CF}$ 27.6	
117.9			$^{1}J_{CF}$ 286	d
			$^{2}J_{CF}$ 33.8	
118.3				e
120.3			$^{1}J_{CF}$ 287	a
			$^{2}J_{CF}$ 27.6	
110.8			$^{1}J_{CF}$ 268	c
			$^{2}J_{CF}$ 38.7	
			$^{2}J_{CF}$ 37.8	

46) (1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol (**67**)



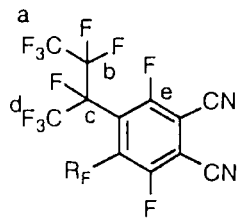
Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{1}H				
1.42	3	d	$^{3}J_{HH}$ 7.0	l
3.04	3	d	$^{3}J_{HH}$ 4.0	j
4.43	1	m		k
4.67	1	m		m
4.85	1	br s		n
7.17 – 7.37	5	m		o
^{19}F				
-80.6	3	m		a
-87.9	3	m		d
-97.0	1	m		h
-125.9 to -129.6	2	m		c
-134.3	1	m		f
-155.5	0.5	m		i, minor
-162.6	0.5	m		i, major
-189.5	0.5	m		b, minor
-190.3	0.5	m		b, major

47) 3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile (**68**).



Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-72.0 - -73.2	3	m		d
-80.1	3	m		a
-84.2	0.5	m		f, major
-88.1	0.5	m		f, minor
-96.1	0.5	m		h, major
-99.8	0.5	m		h, minor
-124.1	0.5	m		g, major
-125.8	0.5	m		g, minor
-116.5 - -122.3	2	m		b
-181.3	1	m		c
^{13}C				
94.3		dm	$^{1}J_{CF}$ 212	c
117.9		qt	$^{1}J_{CF}$ 287 $^{2}J_{CF}$ 33.8	a
120.2		qd	$^{1}J_{CF}$ 290 $^{2}J_{CF}$ 26.5	d

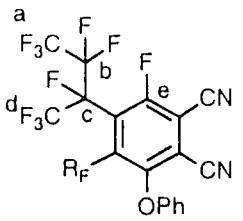
48) 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile (**69**).



$R_F = CF_3CF_2CF(CF_3)$

Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-73.5	6	m		d
-80.6	6	m		a
-84.9	1	m		e, major
-88.5	1	m		e, minor
-116.5 - -122.5	4	m		b
-172.5	1	m		c, major
-182.0	1	m		c, minor
^{13}C				
93.9		dpm	$^1J_{CF}$ 213 $^2J_{CF}$ 38.8	c
117.9		qt	$^1J_{CF}$ 288 $^2J_{CF}$ 34.1	a
120.2		qd	$^1J_{CF}$ 288 $^2J_{CF}$ 27.6	d

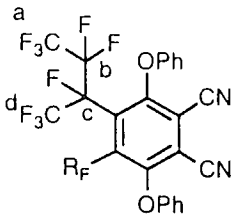
49) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile (**70**)



$R_F = CF_3CF_2CF(CF_3)$

Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-70.9	3		m	d, minor
-73.3	3		m	d, major
-80.2	6		m	a
-80.3	0.5		m	e, minor
-86.3	0.5		m	e, major
-116.4 - -120.3	4		m	b
-172.9	1		m	c, major
-182.2	1		m	c, minor

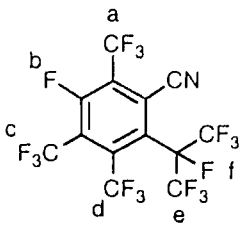
50) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile (**71**).



$R_F = CF_3CF_2CF(CF_3)$

Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-70.4 - -79.7	6		m	d
-79.8 - -80.7	6		m	a
-112.2 - -119.5	4		m	b
-160.6	2		m	c
-179.4	2		m	c

51) 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile (**72**).



Chemical Shift	Intensity	Multiplicity	Coupling (Hz)	Assignment
^{19}F				
-56.5	6	m		a, d
-57.2	3	d	$^4J_{FF}$ 28.0	c
-69.2	6	s		e
-100.6	1	sept	$^4J_{FF}$ 26.0	b
-163.5	1	q	$^4J_{FF}$ 54.0	f

Appendix B Mass Spectrometry.

Chapter II

1)	3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 355	(3)
2)	3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 541	(4)
3)	2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 357	(5)
4)	2,6-dibutyl-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 395	(6)
5)	6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 357	(7)
6)	2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 395	(8)
7)	4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione	RMM 459	(9)
8)	6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 341	(10)
9)	2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine	RMM 377	(11)
10)	3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine	RMM 435	(12)
11)	2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 339	(13)
12)	2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 359	(14)
13)	3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine	RMM 351	(15)
14)	diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine	RMM 372	(18)
15)	{6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}diethylamine	RMM 425	(19)
16)	benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine	RMM 406	(20)

Chapter III

17)	19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene	RMM 682	(35)
18)	25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene	RMM 770	(37)
19)	26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene	RMM 806	(39)
20)	11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20),15,17-hexaene	RMM 708	(42)
21)	2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene	RMM 752	(43)
22)	2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol	RMM 360	(44a)
23)	{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine	RMM 659	(44)
24)	14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene	RMM 681	(45)
25)	3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine	RMM 884	(46)
26)	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane	RMM 513	(47)

27)	methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine	RMM 1074	**(48)**
28)	3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane	RMM 1122	**(49)**

Chapter IV

29)	4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine	RMM 452	**(50)**
30)	2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine	RMM 302	**(51)**
31)	2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine	RMM 314	**(52)**
32)	5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine	RMM 326	**(53)**
33)	6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine	RMM 654	**(54)**
34)	4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine	RMM 464	**(55)**
35)	4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine	RMM 618	**(56)**
36)	4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine	RMM 926	**(57)**
37)	{4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine	RMM 505	**(58)**
38)	{4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine	RMM 539	**(59)**
39)	2,5,6-trifluoro-4-methoxypyrimidine	RMM 164	**(60)**
40)	2,5-difluoro-6-hydroxy-4-methoxypyrimidine	RMM 162	**(61)**

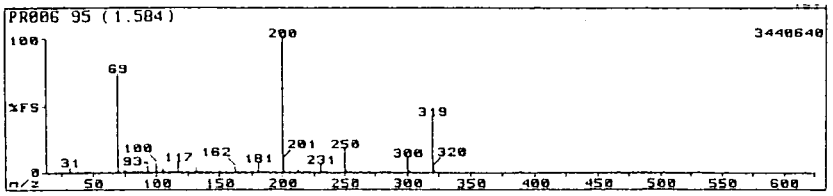
41)	6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine	RMM 350	(62)
42)	4,6-bis(tert-butoxy)-2,5-difluoropyrimidine	RMM 260	(63)

Chapter V

43)	2,3,5,6-tetrafluoro-4-trifluoromethylpyridine	RMM 219	(64)
44)	3,5,6-trifluoro-2-phenoxy-4-trifluoromethylpyridine	RMM 293	(65)
45)	2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine	RMM 369	(66)
46)	(1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol	RMM 514	(67)
47)	3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile	RMM 400	(68)
48)	4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile	RMM 600	(69)
49)	4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile	RMM 674	(70)
50)	4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile	RMM 748	(71)
51)	3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile	RMM 493	(72)

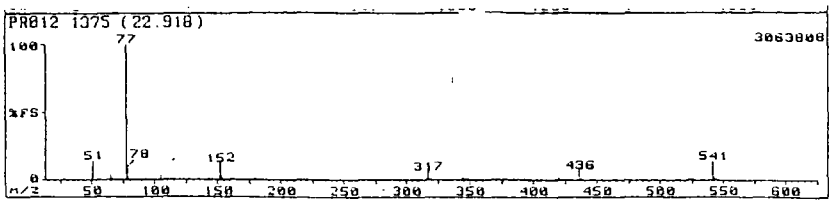
1) 3-fluoro-2,5,6-trimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 355 (3)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.15	100	2.23	168	0.14	236	0.17
28	2.94	101	0.09	169	0.41	243	0.61
31	4.79	104	0.11	173	0.07	248	0.06
32	1.37	105	1.81	174	0.58	249	0.11
40	0.12	106	0.14	179	0.66	250	2.96
44	0.07	107	0.10	180	0.45	251	0.25
44	0.41	110	0.21	181	4.24	255	0.13
47	0.05	111	0.05	182	0.32	261	0.19
50	2.48	112	0.75	185	0.07	262	4.07
51	0.12	114	0.25	186	0.64	263	0.37
55	0.78	116	0.09	188	0.08	267	0.09
61	0.08	116	0.30	192	0.22	274	0.13
62	0.46	117	6.63	193	2.84	280	0.16
67	0.08	118	0.37	194	0.24	281	1.79
69	100.00	119	0.45	198	0.48	282	0.34
70	0.93	124	4.09	199	0.19	293	0.07
73	0.14	125	0.22	200	3.29	300	0.61
74	1.42	129	0.58	201	0.25	312	0.75
75	0.13	131	1.61	204	0.05	313	0.09
76	0.47	132	0.10	205	0.71	319	0.35
78	0.05	136	0.89	206	0.05	331	0.23
79	0.50	138	0.25	207	0.06	332	0.04
80	0.06	141	0.23	211	0.16	349	0.62
81	0.71	143	0.84	212	3.49	350	11.65
82	0.06	148	1.02	213	0.30	351	0.99
84	0.20	149	0.08	216	0.04	362	0.13
85	0.10	150	0.21	217	0.75	381	0.14
86	1.22	155	1.61	219	0.10	400	1.59
88	0.16	156	0.09	223	0.12	401	0.18
92	0.34	160	0.09	224	2.66	450	0.50
93	5.37	161	0.29	225	0.23	451	0.05
94	0.20	162	2.64	229	0.09	469	0.17
97	0.08	163	0.19	230	0.28		
98	1.07	166	0.14	231	8.13		
99	0.17	167	1.26	232	0.65		

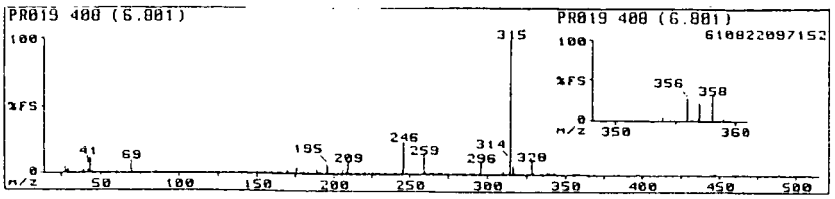
2) 3-fluoro-2,5,6-triphenoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine RMM 541 (4)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
256	0.34	310	0.25	364	0.02	420	1.38
257	0.31	311	0.14	365	0.02	421	0.69
258	0.28	312	0.19	366	0.12	422	0.12
259	0.25	313	0.16	367	0.37	423	0.02
260	0.11	314	0.07	368	0.31	424	0.03
261	0.43	315	0.13	369	0.07	426	0.13
262	0.53	316	0.10	370	0.30	427	0.05
263	0.22	317	6.35	371	0.14	428	0.20
264	0.14	318	1.06	372	0.18	429	0.39
265	0.05	319	0.36	373	0.14	430	0.12
266	0.99	320	0.25	374	0.05	431	0.02
267	0.24	321	1.38	375	0.05	434	0.03
268	0.16	322	0.52	376	0.13	436	7.42
269	0.96	323	0.21	377	0.16	437	1.53
270	0.61	324	0.21	378	0.11	438	0.19
271	0.78	325	0.15	379	0.44	439	0.02
272	0.18	326	0.34	380	0.16	444	0.06
273	0.56	327	0.26	381	0.04	445	0.12
274	0.72	328	0.11	382	0.05	446	0.44
275	0.18	329	0.33	383	0.01	447	1.01
276	0.17	330	0.28	384	0.04	448	1.99
277	0.12	331	0.29	385	0.01	449	0.45
278	0.48	332	0.19	386	0.13	450	0.06
279	0.53	333	0.45	387	0.05	451	0.01
280	0.34	334	0.12	388	0.53	452	0.01
281	0.33	335	0.05	389	0.11	453	0.10
282	0.48	336	0.05	390	0.08	454	0.05
283	0.19	337	0.05	391	0.04	455	0.02
284	0.12	338	0.15	392	0.61	460	0.01
285	0.11	339	0.19	393	0.17	462	0.01
286	0.17	340	0.42	394	0.07	463	0.07
287	0.10	341	0.09	395	0.03	464	0.97
288	0.05	342	0.64	396	0.12	465	0.21
289	1.90	343	0.40	397	0.03	466	0.04
290	0.43	344	0.27	398	0.74	467	0.01
291	0.19	345	2.47	399	0.16	470	0.01
292	0.16	346	0.36	400	0.18	471	0.02
293	0.07	347	0.23	401	0.07	472	0.04
294	0.08	348	0.19	402	0.08	473	0.01
295	0.08	349	1.63	403	0.07	484	0.02
296	0.20	350	0.58	404	0.03	487	0.02
297	0.53	351	0.31	405	0.02	494	0.04
298	0.23	352	0.20	406	0.09	495	0.01
299	0.25	353	0.12	407	0.04	500	0.01
300	0.15	354	0.06	408	0.99	503	0.02
301	0.61	355	0.31	409	0.13	504	0.01
302	0.45	356	0.15	410	0.06	512	0.02
303	0.43	357	0.03	411	0.01	513	0.43
304	0.19	358	0.47	412	0.00	514	0.12
305	0.11	359	0.27	414	0.00	515	0.02
306	0.09	360	0.57	416	0.27	521	0.02
307	0.06	361	0.15	417	0.06	522	1.24
308	0.16	362	0.04	418	1.82	523	0.33
309	0.14	363	0.01	419	0.55	524	0.28

3) 2-butyl-3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

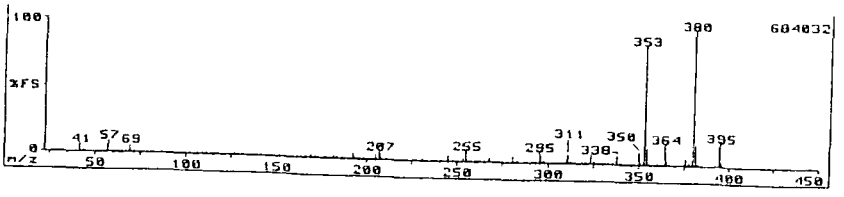
RMM 357 (5)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
244	0.98	272	0.19	303	0.10	341	0.08
245	3.76	273	1.04	304	0.04	342	1.84
246	24.61	274	0.36	306	0.03	343	0.20
247	2.26	275	0.12	307	0.02	352	0.03
248	0.20	276	0.64	308	0.10	354	0.13
249	0.26	277	0.53	309	0.23	355	0.05
250	0.40	278	0.10	310	2.94	356	0.79
251	0.23	279	0.02	311	0.29	357	0.56
252	0.63	281	0.04	312	0.02	358	0.92
253	0.31	282	0.07	314	11.87	359	0.12
254	0.21	283	0.23	315	100.00	384	0.01
255	0.41	284	0.35	316	7.03	396	0.02
256	0.33	285	0.27	317	0.36	398	0.02
257	0.48	286	0.08	318	0.09	426	0.03
258	0.63	287	0.34	320	0.02	444	0.01
259	14.65	288	0.16	321	0.05	446	0.07
260	1.59	289	0.08	322	0.11	447	0.02
261	0.11	290	0.42	323	0.05	458	0.01
262	0.10	291	0.07	326	0.27	460	0.03
263	0.09	292	0.02	327	0.51	464	0.06
264	1.62	294	0.23	328	9.81	465	0.18
265	0.30	295	0.16	329	2.25	466	0.04
266	0.19	296	8.79	330	0.18	488	0.26
267	0.10	297	0.99	334	0.03	489	0.06
268	0.31	298	0.14	336	0.07	506	0.01
269	0.94	300	0.04	338	1.32	507	0.15
270	1.76	301	0.53	339	0.40	508	0.05
271	1.94	302	0.83	340	0.54		

4) 2,6-dibutyl-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

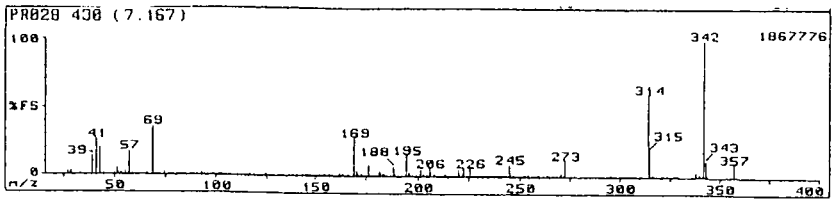
RMM 395 (6)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
250	0.43	283	0.59	317	0.29	350	10.18
251	0.20	284	1.96	318	0.43	351	2.39
252	0.99	285	0.29	319	0.27	352	2.05
253	1.15	286	0.24	320	0.33	353	88.62
254	2.71	287	0.07	321	0.22	354	12.87
255	7.82	288	0.16	322	1.51	355	0.96
256	1.17	289	0.15	323	1.18	356	0.16
257	0.24	290	0.47	324	6.96	358	0.21
258	0.80	291	0.41	325	1.99	359	0.10
259	0.64	292	1.80	326	0.76	360	0.38
260	0.65	293	0.70	327	0.17	361	1.23
261	1.14	294	0.92	328	0.11	362	0.50
262	1.02	295	7.56	329	0.05	363	0.29
263	0.35	296	5.99	330	0.10	364	15.12
264	0.25	297	2.03	331	0.13	365	9.24
265	0.68	298	0.54	332	0.34	366	1.62
266	1.37	299	0.17	333	0.20	367	0.15
267	2.11	300	0.11	334	0.44	374	0.26
268	1.74	302	0.01	335	0.10	375	0.23
269	2.04	303	0.09	336	2.40	376	5.61
270	0.50	304	0.28	337	5.91	377	1.05
271	0.22	305	0.15	338	7.07	378	1.11
272	0.33	306	0.34	339	2.27	379	1.63
273	0.18	307	0.23	340	1.37	380	100.00
274	0.53	308	0.38	341	0.21	381	16.02
275	0.48	309	0.92	342	0.38	382	1.36
276	1.71	310	2.99	343	0.11	383	0.11
277	0.87	311	6.81	344	0.39	392	0.13
278	1.04	312	1.47	345	0.19	393	0.24
279	0.96	313	0.15	346	0.65	394	16.03
280	0.78	314	0.03	347	0.47	395	17.22
281	4.64	315	0.12	348	0.52	396	2.92
282	0.79	316	0.76	349	0.27	397	0.27

5) 6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 357 (7)



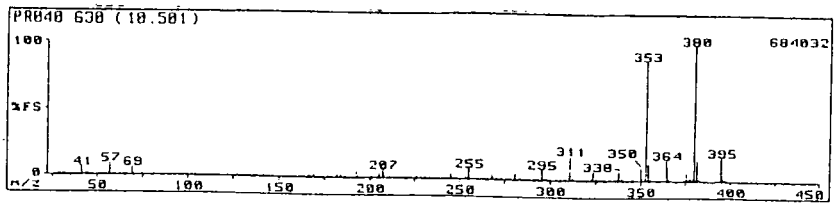
Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
26	0.02	99	2.30	158	1.04	214	2.48
27	2.99	100	1.37	159	0.48	215	0.61
28	1.56	101	0.74	161	1.25	216	0.21
29	4.11	102	0.25	162	2.73	217	0.20
31	0.93	103	0.17	163	1.59	218	0.49
32	0.47	104	0.08	164	1.12	219	1.00
33	0.26	105	1.27	165	0.39	220	5.15
37	0.22	106	0.89	166	0.19	221	2.25
39	13.38	107	0.60	167	0.49	222	0.63
41	26.10	108	0.26	169	23.07	223	5.76
43	20.18	109	0.19	170	3.95	224	0.73
44	0.85	110	0.37	171	1.86	225	0.65
45	0.36	111	0.58	172	1.04	226	5.87
46	0.95	112	0.87	173	2.36	227	1.06
47	0.45	113	0.82	174	1.07	228	0.27
48	0.04	114	0.49	175	1.45	229	0.08
50	1.91	115	0.12	176	8.94	230	0.14
51	4.61	117	2.43	177	1.40	231	0.39
52	1.07	118	0.26	178	0.31	232	0.96
53	2.11	119	0.93	179	0.17	233	1.07
55	2.62	120	0.33	180	0.50	234	0.50
57	17.54	121	0.16	181	1.51	235	0.08
58	0.69	123	0.69	182	3.03	236	0.08
59	0.54	124	1.62	183	2.10	237	0.59
61	1.27	125	1.41	184	2.30	238	0.86
62	0.68	126	0.65	185	0.59	239	0.19
63	1.15	127	0.93	186	0.76	240	0.12
64	0.60	128	0.25	187	1.11	241	0.14
65	0.84	131	1.14	188	7.24	242	0.03
66	0.12	132	1.10	189	1.69	243	0.20
69	35.53	133	0.90	190	0.38	244	0.95
70	0.71	134	0.29	191	0.25	245	8.94
71	0.24	136	0.25	192	0.20	246	2.33
72	0.12	138	1.74	193	0.75	247	1.12
75	3.30	138	0.95	194	0.69	248	0.17
76	0.70	139	0.41	195	15.79	249	0.29
77	0.63	140	0.24	196	2.66	250	0.50
78	0.22	141	0.12	197	0.65	251	0.30
79	0.27	143	0.24	198	0.26	252	1.56
81	2.15	143	1.37	199	1.12	253	1.10
82	0.69	145	1.59	200	2.19	254	2.54
83	0.51	145	2.41	201	0.87	255	0.64
84	0.26	146	1.12	202	4.61	256	0.25
85	0.80	147	0.58	203	2.11	257	1.45
87	0.45	148	0.10	204	0.42	258	0.38
88	0.72	150	0.24	205	2.00	259	1.82
89	0.21	151	1.55	206	6.09	260	0.21
90	0.15	152	1.15	207	2.77	262	0.11
91	0.10	153	1.63	208	2.12	264	1.67
93	2.74	154	1.38	209	2.32	265	0.17
94	0.32	155	1.75	210	0.22	266	0.11
95	0.78	156	1.36	211	0.20	267	0.09
96	0.42	157	1.29	212	0.96	268	0.10
97	0.19	157	2.10	213	0.50	269	0.30

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
270	1.64	289	0.06	308	0.06	334	0.02
271	2.62	290	0.05	310	1.40	336	0.13
272	0.99	291	0.02	311	0.15	338	3.89
273	11.90	292	0.01	314	60.53	339	0.45
274	1.43	294	0.34	315	19.52	340	2.70
275	0.17	295	0.32	316	2.22	341	1.18
276	1.40	296	2.08	317	0.14	342	100.00
277	0.22	297	0.26	318	0.11	343	11.40
278	0.07	298	0.04	320	0.02	344	0.58
281	0.07	300	0.30	321	0.08	354	0.10
282	0.03	301	0.27	322	0.90	356	0.59
283	0.09	302	0.42	323	0.88	357	9.54
284	0.71	303	0.04	324	0.11	358	1.06
285	0.14	304	0.42	326	0.92	359	0.07
286	0.09	305	0.06	327	0.16		
287	0.21	306	0.04	328	0.99		
288	0.50	307	0.02	329	0.11		

6) 2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 395

(8)

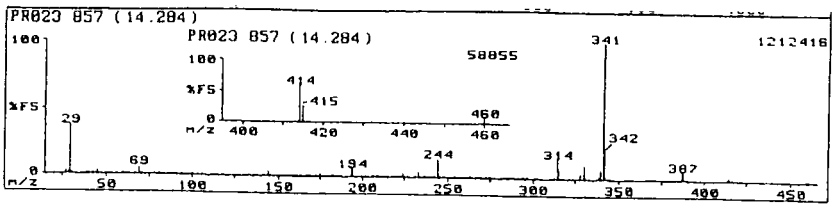


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
250	0.43	283	0.59	317	0.29	350	10.18
251	0.20	284	1.96	318	0.43	351	2.39
252	0.99	285	0.29	319	0.27	352	2.05
253	1.15	286	0.24	320	0.33	353	88.62
254	2.73	287	0.07	321	0.22	354	12.87
255	7.82	288	0.16	322	1.51	355	0.96
256	1.17	289	0.16	323	1.18	356	0.16
257	0.24	290	0.47	324	6.96	358	0.21
258	0.80	291	0.41	325	1.99	359	0.10
259	0.64	292	1.80	326	0.76	360	0.38
260	0.65	293	0.70	327	0.17	361	1.23
261	1.14	294	0.92	328	0.11	362	0.50
262	1.02	295	7.56	329	0.05	363	0.29
263	0.35	296	5.99	330	0.30	364	15.12
264	0.25	297	2.03	331	0.18	365	9.24
265	0.68	298	0.54	332	0.14	366	1.62
266	1.37	299	0.17	333	0.20	367	0.15
267	2.11	300	0.11	334	0.44	374	0.26
268	3.74	302	0.03	335	0.30	375	0.23
269	2.04	303	0.09	336	2.40	376	5.61
270	0.50	304	0.28	337	5.91	377	1.05
271	0.22	305	0.15	338	7.07	378	3.11
272	0.33	306	0.14	339	2.27	379	3.63
273	0.18	307	0.23	340	1.37	380	100.00
274	0.58	308	0.38	341	0.21	381	16.02
275	0.48	309	0.92	342	0.38	382	1.16
276	1.71	310	2.99	343	0.11	383	0.11
277	0.37	311	6.81	344	0.39	392	0.13
278	1.04	312	1.47	345	0.19	393	0.24
279	0.96	313	0.16	346	0.65	394	16.02
280	0.78	314	0.03	347	0.47	395	17.22
281	4.64	315	0.12	348	0.52	396	2.92
282	0.79	316	0.76	349	0.27	397	0.27

7) 4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione

RMM 459

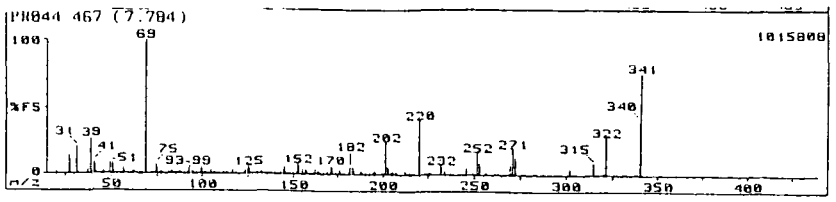
(9)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.02	94	0.13	164	0.46	232	0.07
26	0.26	95	0.08	165	0.05	233	4.20
27	3.34	96	0.04	167	0.33	234	0.32
28	1.90	98	0.08	168	0.54	236	0.09
29	36.49	99	0.65	169	0.22	237	0.42
30	1.18	100	0.19	170	0.06	238	0.07
31	1.17	101	0.06	172	0.19	240	0.13
32	0.79	102	0.02	173	0.03	241	0.12
36	0.03	103	0.02	174	0.44	242	0.48
38	0.03	104	0.05	175	3.29	243	0.46
39	0.04	105	0.19	176	0.68	244	13.26
40	0.06	106	0.50	177	0.09	245	1.84
41	0.16	107	0.05	179	0.28	246	0.13
42	0.23	108	0.02	180	0.38	247	0.04
43	1.50	111	0.12	181	0.46	248	0.03
44	1.01	112	0.12	182	0.45	249	0.08
45	2.66	113	0.24	183	2.30	250	0.10
46	0.27	114	0.17	184	0.14	252	0.07
47	0.34	115	0.04	186	0.19	253	0.58
50	0.11	117	0.55	187	0.21	254	0.11
51	0.20	118	0.14	188	0.16	255	0.05
52	0.02	119	0.09	191	0.05	256	0.06
53	0.12	120	0.05	193	0.87	257	0.04
55	0.05	124	0.60	194	5.56	259	0.29
56	0.18	125	0.16	195	1.41	260	0.02
57	0.09	126	0.12	196	0.22	261	1.11
59	0.06	127	0.03	198	0.21	262	0.27
60	0.05	130	0.44	199	1.67	263	2.03
61	0.15	131	0.24	200	0.40	264	0.61
62	0.02	132	0.14	201	0.19	265	0.07
63	0.03	133	0.50	202	0.13	267	0.08
64	0.02	134	0.04	203	0.04	268	0.11
67	0.03	136	0.16	205	0.83	269	0.02
69	6.17	137	0.35	206	1.96	270	0.09
70	0.32	138	0.07	207	0.29	271	0.21
71	0.08	141	0.03	208	0.04	272	0.63
73	0.59	143	0.30	209	0.08	273	0.29
74	0.13	144	4.35	210	0.09	274	0.19
75	0.55	145	0.71	211	0.27	275	0.08
76	0.17	146	0.07	212	0.41	276	0.15
77	0.02	148	0.33	213	0.48	277	0.03
78	0.02	149	0.62	214	0.75	281	0.05
79	0.05	150	0.16	215	0.09	282	0.06
80	0.11	151	0.10	217	0.45	283	0.04
81	0.07	152	0.04	218	0.46	284	0.01
82	0.06	153	0.04	219	0.09	286	0.07
83	0.03	155	0.55	220	0.15	287	0.61
86	0.11	156	0.26	222	2.34	288	0.11
87	0.13	157	0.11	223	0.16	289	0.04
88	0.75	158	0.03	224	3.27	290	0.08
89	0.05	159	0.03	225	1.20	291	0.09
90	0.02	161	0.63	226	0.72	292	0.19
91	0.02	162	0.22	227	0.06	293	0.14
93	0.51	163	1.21	231	0.16	294	2.26

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
295	0.27	317	0.07	342	20.86	384	0.06
296	0.13	319	0.02	343	2.28	396	1.67
297	0.03	320	0.06	344	0.17	397	6.25
300	0.80	322	0.60	345	0.03	398	0.86
301	0.06	323	0.19	346	0.01	399	0.05
302	0.78	324	0.03	354	0.04	413	0.11
303	0.17	326	0.23	356	0.04	414	2.91
304	0.04	327	0.30	358	1.06	415	1.27
310	0.34	328	1.44	359	0.17	416	0.10
311	0.35	330	10.64	366	0.50	440	0.10
312	0.66	331	0.94	367	0.06	459	0.05
313	1.92	333	2.55	368	0.52	460	0.19
314	14.44	339	0.50	369	0.14	461	0.06
315	7.77	340	7.26	370	1.28		
316	0.70	341	100.00	371	0.16		

8) 6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine RMM 341 (10)

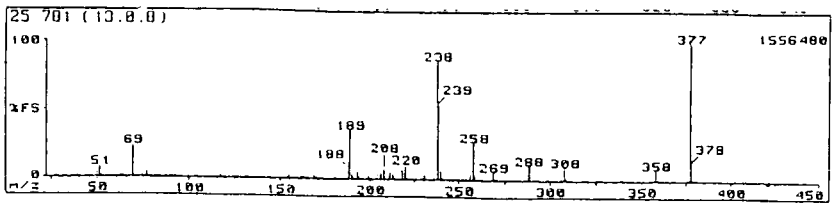


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	2.12	81	2.92	136	1.40	190	0.18
24	1.01	83	2.47	137	2.39	191	0.14
25	1.43	84	0.76	138	1.22	192	0.55
26	6.43	85	1.36	139	0.42	193	1.17
27	13.71	86	1.34	140	0.13	194	2.47
28	9.98	87	2.14	141	0.28	195	2.77
29	0.74	88	1.34	142	1.09	196	1.53
31	20.77	89	0.43	143	3.20	197	0.11
32	1.31	90	0.29	144	4.46	199	0.67
33	0.95	91	0.39	145	5.39	199	1.06
35	0.13	92	1.89	146	1.16	200	2.17
36	0.37	93	5.42	147	0.28	202	24.50
37	2.47	94	1.56	148	0.53	203	5.77
38	3.86	95	1.92	149	1.39	204	1.53
39	27.02	96	0.59	150	2.04	205	2.24
40	1.99	97	0.50	151	3.78	206	2.95
41	8.87	98	2.09	152	8.17	207	1.71
42	0.52	99	5.44	153	5.54	208	0.37
43	0.50	100	3.45	154	1.44	212	2.92
44	0.91	101	1.81	155	3.50	213	1.25
45	0.61	102	0.91	156	3.91	214	1.02
46	3.07	103	0.59	157	2.72	215	0.17
47	0.84	104	1.22	158	1.03	217	0.27
48	0.47	105	3.40	159	0.13	220	40.73
49	0.36	106	2.42	160	0.36	223	0.37
50	8.27	107	1.66	161	1.79	225	1.40
51	7.66	108	0.60	162	3.50	226	2.37
52	1.36	109	0.26	163	2.57	226	0.64
53	1.03	110	0.50	164	2.17	227	1.28
54	0.18	111	1.21	165	0.36	230	0.34
55	0.83	112	1.86	166	0.24	232	6.96
56	1.40	113	1.52	167	0.87	234	2.67
57	5.04	114	0.80	168	1.86	237	0.49
57	2.12	115	0.21	169	3.88	238	1.41
59	1.03	116	1.33	170	6.38	242	0.11
59	0.44	117	3.53	171	5.57	243	0.30
61	1.17	118	1.37	172	4.96	244	0.60
62	1.94	119	2.12	173	1.08	245	0.72
63	2.72	120	0.68	174	2.34	246	5.22
63	1.06	121	0.50	175	3.65	249	0.12
64	1.29	122	0.71	176	3.73	250	0.64
65	0.77	123	2.19	177	0.72	251	1.27
66	1.02	124	4.01	178	0.18	252	16.13
67	0.22	125	6.07	179	0.42	253	9.17
69	100.00	126	3.65	180	1.37	256	0.28
71	0.72	127	0.86	181	3.68	257	1.76
72	0.12	128	0.18	182	6.30	261	0.06
74	1.94	129	0.62	183	5.97	262	0.32
75	5.38	130	1.61	184	4.03	263	0.12
75	4.18	131	2.22	185	0.81	264	0.43
76	1.84	132	2.37	186	1.27	268	0.11
77	0.54	133	1.54	187	2.75	270	7.96
78	0.47	134	0.72	188	3.20	271	19.46
79	0.71	135	0.47	189	0.69	272	12.20

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
276	0.69	297	0.04	321	2.12	372	0.15
277	1.04	300	0.08	322	27.82	378	0.08
281	0.09	301	0.67	326	1.21	380	0.16
282	0.75	302	4.96	328	0.08	389	0.10
283	0.29	303	1.05	332	0.02	390	0.16
284	1.02	304	0.10	338	0.11	409	0.17
287	0.08	306	0.06	339	1.11	410	0.26
288	0.40	308	0.05	340	41.13	416	0.02
291	0.49	314	0.66	341	75.40	431	0.03
294	0.14	315	9.77	352	0.14		
296	0.08	320	0.35	360	0.05		

9) 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine

RMM 377 (11)

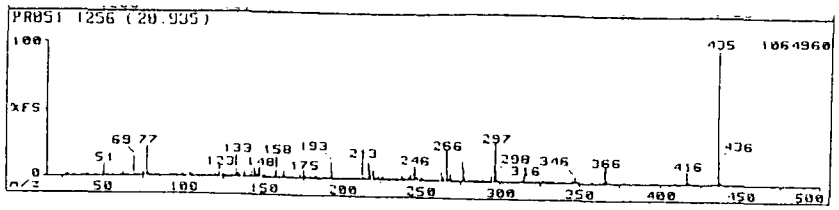


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
26	0.06	94	0.61	150	0.31	204	0.51
27	0.19	95	0.23	151	0.59	205	1.78
28	0.28	96	0.15	152	0.12	206	1.49
31	0.44	98	0.60	153	0.10	207	6.97
32	0.11	99	1.35	154	0.43	208	7.61
33	0.02	100	1.07	155	4.21	209	1.01
36	0.02	101	0.19	156	0.64	210	0.31
37	0.10	102	0.12	157	0.53	211	3.35
38	0.32	103	1.23	158	1.34	212	6.05
39	1.33	104	0.80	159	0.29	213	1.96
40	0.08	105	1.17	160	0.25	214	0.51
44	0.08	106	0.61	161	1.58	215	0.05
45	0.03	107	0.57	162	2.93	216	0.24
46	0.20	108	0.18	163	1.71	217	0.49
49	0.16	109	0.17	164	0.31	218	7.43
50	4.93	110	0.31	165	0.49	219	4.93
51	8.16	111	0.60	166	0.16	220	10.36
52	1.43	112	0.60	167	1.15	221	1.17
53	0.10	113	0.24	168	2.30	222	0.30
55	0.27	114	0.15	169	2.85	223	0.61
56	0.17	115	0.65	170	1.20	224	1.25
57	0.64	117	3.16	171	0.21	225	0.63
58	0.05	118	0.52	172	0.10	226	0.16
59	0.04	119	0.40	173	0.36	227	0.29
61	0.49	120	0.47	174	1.00	228	0.07
62	1.09	121	0.04	175	1.40	229	0.41
63	1.76	122	0.17	176	0.81	230	2.02
64	0.29	123	1.30	177	0.11	231	1.54
65	0.07	124	1.17	178	0.08	232	1.12
68	0.31	125	0.24	179	0.41	233	0.11
69	22.89	126	0.08	180	1.32	235	0.07
70	0.52	127	0.29	181	2.45	236	1.10
72	0.05	129	1.07	182	1.25	237	1.23
73	0.17	129	1.07	183	0.32	238	86.32
74	2.07	130	0.32	184	0.12	239	53.95
75	2.11	131	0.86	185	0.89	240	6.73
76	1.89	132	0.29	186	1.92	241	0.54
77	1.79	133	0.04	187	2.24	242	0.82
78	0.26	134	0.30	188	6.91	243	1.00
79	0.13	135	0.43	189	16.12	244	0.17
80	0.44	136	0.91	190	4.18	245	0.06
81	0.95	137	0.60	191	0.79	247	0.07
82	0.23	138	0.46	192	1.37	248	0.22
83	0.07	139	0.13	193	5.53	249	0.78
84	0.05	140	0.10	194	2.01	250	1.00
85	0.14	141	0.13	195	0.30	251	0.31
86	0.39	142	0.51	196	0.08	252	0.03
87	0.75	143	1.59	197	0.08	254	0.11
88	0.46	144	0.97	198	0.17	255	0.90
89	0.25	145	0.41	199	1.05	256	2.80
90	0.12	146	0.13	200	3.19	257	5.19
91	0.04	147	0.46	201	0.70	258	27.11
92	0.59	148	0.52	202	0.10	259	3.49
93	2.04	149	0.47	203	0.13	260	0.35

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
261	0.45	279	0.01	298	0.07	328	0.05
262	0.49	280	0.06	299	0.04	338	1.40
263	0.45	281	0.47	300	0.08	339	0.55
264	0.08	282	0.09	306	0.52	340	0.08
267	0.24	283	0.02	307	2.15	356	0.08
268	0.71	285	0.01	308	9.47	357	0.11
269	5.99	286	0.05	309	1.55	358	3.22
270	1.78	287	0.72	310	0.14	359	1.28
271	0.20	288	11.12	312	0.03	360	0.11
271	0.06	289	10.72	318	0.12	376	0.66
274	0.13	290	1.40	319	0.05	377	100.00
275	0.04	291	0.12	320	0.12	378	12.41
276	0.28	292	0.05	325	0.05	379	0.98
277	0.22	293	0.05	326	0.19	380	0.08
278	0.03	294	0.04	327	0.16		

10) 3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine

RMM 435 (12)

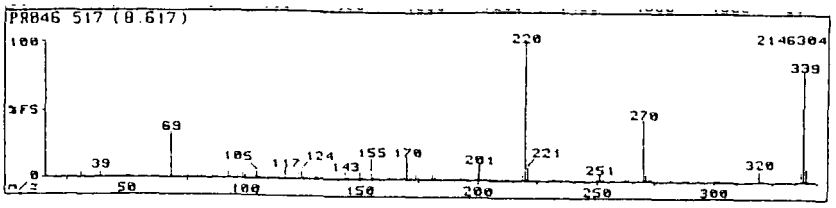


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.10	95	0.59	149	2.16	206	0.30
25	0.28	96	0.52	150	1.68	207	0.84
27	1.71	97	0.40	151	2.45	208	0.56
28	2.43	98	0.96	152	0.84	209	0.15
29	0.06	99	2.60	153	0.64	210	0.20
31	0.50	100	1.44	154	0.59	211	1.29
32	0.50	101	0.51	155	0.90	212	1.13
33	0.08	102	0.66	156	2.09	213	15.58
37	0.12	103	2.76	157	5.07	214	1.97
38	0.49	104	3.15	158	5.48	215	0.32
39	2.76	105	1.61	160	0.32	216	0.10
40	0.20	106	1.06	161	1.01	217	12.21
41	0.05	107	0.99	162	1.68	218	7.79
44	0.11	108	0.76	163	5.50	219	2.67
45	0.03	109	2.24	164	1.15	220	6.44
46	0.04	110	1.43	165	0.47	221	1.73
50	2.79	111	1.38	166	0.20	222	0.90
51	9.71	112	1.17	167	1.30	223	1.00
52	1.43	113	1.36	168	1.38	224	1.87
53	0.11	114	0.47	169	1.71	225	1.61
55	0.01	115	0.87	170	0.78	226	2.09
57	0.82	116	0.72	171	0.19	227	1.15
59	0.05	117	1.53	173	3.97	228	1.05
61	0.19	118	1.02	174	1.95	229	0.41
62	1.08	119	2.31	175	5.96	230	0.49
63	2.76	120	3.29	176	1.43	231	1.17
64	0.38	121	0.86	177	0.31	232	1.07
65	0.20	122	0.75	178	0.25	233	0.33
66	0.03	123	7.40	179	0.22	234	0.20
69	14.62	124	1.97	180	0.38	235	0.25
70	0.55	125	2.31	181	0.60	236	0.54
71	0.04	126	0.70	182	2.60	237	0.91
72	0.03	127	2.31	183	1.71	238	1.85
74	2.43	128	0.80	185	0.46	239	2.62
75	3.15	129	0.88	186	0.60	240	0.66
76	3.29	130	0.53	187	2.12	241	0.17
77	23.79	131	1.58	188	0.95	242	1.95
78	1.80	132	3.05	189	1.18	243	3.27
79	0.03	133	6.03	190	0.25	244	2.43
80	0.42	134	2.93	191	0.40	245	5.24
81	1.33	135	2.38	192	0.59	246	11.06
82	0.16	136	1.28	193	12.21	247	10.19
83	0.48	137	1.27	194	5.34	248	1.92
84	0.11	138	4.56	195	1.35	249	1.56
85	0.16	139	1.93	196	0.55	250	1.71
86	0.30	140	0.43	197	0.17	251	1.62
87	1.39	141	0.55	198	1.14	252	0.66
88	0.70	142	0.52	199	0.86	253	0.21
89	1.06	143	6.44	200	1.80	254	0.21
90	0.22	144	6.71	201	1.03	255	0.33
91	0.08	145	2.69	202	0.47	256	1.29
92	0.91	146	0.67	203	0.30	257	1.09
93	2.40	147	5.41	204	0.71	258	1.97
94	1.75	148	7.40	205	0.77	259	0.48

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
260	0.21	291	0.08	325	0.79	364	1.44
261	0.55	292	0.19	326	2.96	365	9.62
262	1.10	293	0.70	327	1.54	366	12.02
263	7.02	294	2.16	328	0.46	367	2.48
264	2.86	295	4.71	329	0.07	368	0.30
265	3.03	296	12.12	330	0.02	370	0.04
266	22.40	297	27.69	331	0.07	376	0.15
267	4.57	298	5.50	332	0.12	377	0.04
268	0.97	299	0.62	333	0.06	378	0.03
269	5.60	300	0.44	334	0.04	384	0.13
270	1.75	301	0.40	336	0.05	385	0.07
271	0.46	302	0.13	337	0.09	394	0.12
272	0.14	304	0.05	338	0.17	395	0.06
273	0.42	305	0.41	339	0.42	396	0.66
274	1.00	306	0.68	340	0.15	397	0.38
275	1.17	307	0.94	342	0.04	398	0.07
276	15.38	308	0.69	343	0.09	403	0.16
277	9.33	309	0.13	344	0.60	409	0.04
278	3.05	311	0.08	345	1.26	414	0.15
279	0.54	312	0.21	346	5.10	415	0.65
280	0.40	313	0.91	347	4.95	416	10.00
281	0.62	314	1.63	348	0.92	417	2.24
282	0.59	315	5.02	349	0.11	418	0.23
283	0.17	316	5.19	350	0.07	434	8.17
284	0.14	317	0.94	351	0.10	435	100.00
285	0.11	318	0.25	356	0.09	436	17.50
286	0.25	319	1.11	357	0.11	437	1.35
287	0.70	320	0.42	358	0.33	438	0.16
288	2.19	321	0.09	359	0.07		
289	1.68	323	0.07	362	0.04		
290	0.18	324	0.18	363	0.27		

11) 2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 339 (13)

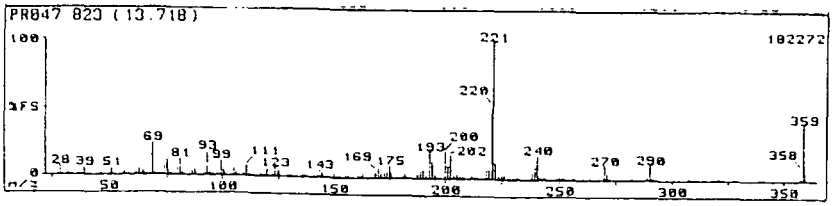


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.04	90	0.04	151	2.09	217	0.34
25	0.03	92	0.91	152	0.20	218	0.76
26	0.18	93	4.44	154	1.19	219	5.25
27	0.24	94	0.57	155	5.15	220	100.00
28	0.94	95	0.26	156	1.51	221	10.02
29	0.03	96	0.19	157	0.26	222	0.50
31	3.32	97	0.03	158	0.11	223	1.25
32	0.38	98	1.22	160	0.13	224	0.39
33	0.11	99	3.77	161	0.82	225	0.53
36	0.07	100	2.46	162	1.61	226	0.07
37	0.95	101	0.44	163	0.58	230	2.17
38	2.28	102	0.08	164	0.13	231	0.60
39	5.82	103	0.54	165	0.04	232	2.21
40	0.24	104	1.72	167	0.87	233	0.23
41	0.04	105	5.15	168	2.42	235	0.03
42	0.02	106	1.73	169	3.77	236	0.07
43	0.03	107	0.21	170	16.41	237	0.37
44	0.18	108	0.11	171	1.42	238	0.17
45	0.17	110	1.01	172	0.19	239	0.10
46	0.47	111	1.00	173	0.95	241	0.03
48	0.03	112	1.46	174	4.48	242	0.15
49	0.30	113	0.54	175	2.08	243	0.40
50	2.86	114	0.21	176	0.19	244	0.25
51	2.27	117	7.79	177	0.02	245	0.02
52	0.20	118	0.94	179	0.43	248	0.24
55	0.69	119	1.16	180	2.21	250	3.96
56	0.69	120	0.53	181	3.96	251	5.01
57	0.81	121	0.06	182	2.42	252	0.52
58	0.06	123	5.10	183	0.21	253	0.04
61	0.85	124	5.44	185	0.59	255	0.54
62	0.73	125	1.93	186	0.75	256	0.24
63	0.80	126	0.37	187	0.55	257	0.05
64	0.79	127	0.09	188	1.23	261	0.07
65	0.18	129	0.48	189	0.46	262	0.06
66	0.02	130	2.76	190	0.04	263	0.02
69	33.97	131	1.67	192	1.18	268	0.78
70	0.58	132	1.15	193	2.00	270	45.23
71	0.03	133	0.13	194	1.23	271	4.44
72	0.02	134	0.08	195	0.11	272	0.25
74	2.05	135	0.69	199	2.78	273	0.05
75	2.40	136	1.44	200	6.01	274	0.25
76	0.86	137	0.98	201	11.26	275	0.06
77	0.16	138	0.24	202	1.26	276	0.02
78	0.03	139	0.15	203	0.21	280	0.66
79	0.66	141	0.52	204	0.24	281	0.11
80	1.71	142	0.70	205	2.55	282	0.07
81	2.21	143	6.15	206	0.99	287	0.09
82	0.49	144	1.55	207	0.11	288	0.15
83	0.05	145	0.14	208	0.04	289	0.04
85	1.01	146	0.21	210	0.10	293	0.22
86	1.61	147	0.16	211	0.12	294	0.11
87	1.03	148	1.13	212	1.38	300	1.47
88	0.48	149	0.93	213	0.35	301	0.37
89	0.11	150	6.06	214	0.04	302	0.04

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
305	0.02	321	1.10	338	7.97	341	0.34
318	0.04	322	0.07	339	80.92		
320	9.92	337	0.70	340	9.59		

12) 2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 359 (14)

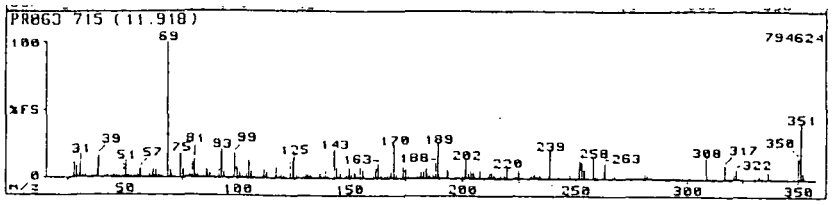


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.18	91	0.75	144	1.69	198	1.50
27	0.50	91	0.15	145	1.52	199	2.28
28	6.85	92	2.98	146	0.50	200	20.37
29	0.11	93	6.78	147	1.16	201	9.83
31	1.89	94	1.20	148	1.40	202	17.13
32	2.19	95	1.91	149	2.84	203	2.70
33	0.30	96	1.02	150	4.04	204	2.90
36	0.18	97	2.91	151	1.79	205	3.69
37	0.48	97	0.83	152	0.97	206	2.28
38	1.21	98	4.99	153	0.80	207	1.77
39	5.69	99	12.38	154	1.12	208	1.84
40	0.49	100	5.13	155	2.53	209	0.54
41	0.08	101	2.14	156	2.91	210	0.60
44	0.76	102	0.71	157	0.83	211	1.09
45	0.44	103	0.90	158	0.54	212	2.74
46	0.49	104	2.42	159	0.26	213	2.05
47	0.13	105	6.04	160	0.56	214	1.83
49	0.30	106	3.13	161	1.75	215	0.26
50	3.58	107	1.00	162	3.13	216	0.32
51	5.90	108	0.24	163	3.51	217	0.38
52	0.79	110	3.41	164	1.20	218	6.81
53	0.16	111	7.30	165	0.42	219	7.06
55	0.30	112	2.91	166	0.26	220	53.37
56	1.63	113	1.31	167	2.53	221	100.00
57	3.48	114	0.46	168	3.48	222	12.92
58	0.21	115	0.22	169	5.30	223	2.53
59	0.23	116	1.44	170	7.87	224	3.34
61	2.19	117	3.37	171	3.69	225	3.44
62	2.84	118	1.87	172	0.75	226	1.44
63	5.06	119	1.64	173	4.49	227	0.43
64	1.49	120	5.55	174	6.53	228	0.09
65	3.41	121	1.04	175	9.55	229	0.97
66	0.67	122	2.53	176	4.00	230	2.32
68	2.19	123	6.78	177	0.53	231	2.13
69	24.44	124	3.65	178	0.21	232	1.59
70	1.69	125	4.95	179	1.33	233	0.32
71	0.65	126	1.20	180	2.28	235	0.14
72	0.57	127	0.29	181	3.13	236	0.91
73	0.45	128	0.58	182	3.41	237	1.14
74	6.43	129	1.50	183	0.97	238	6.21
75	11.24	130	1.70	184	0.38	239	10.67
76	3.16	131	1.15	185	1.22	240	18.68
77	1.97	132	0.97	186	1.61	241	2.42
78	0.55	133	0.19	187	3.37	242	1.67
79	1.02	134	0.48	188	3.86	243	1.98
80	6.04	135	2.67	189	5.79	244	2.28
81	12.78	136	1.47	190	7.06	245	0.69
82	3.02	137	1.40	191	2.24	247	0.18
83	0.61	138	0.89	192	2.24	248	0.52
85	2.21	139	0.44	193	20.79	249	2.15
86	3.79	140	0.59	194	12.64	250	3.09
87	5.34	141	1.12	195	2.98	251	1.62
88	2.16	142	1.46	196	0.41	252	1.41
89	0.91	143	5.48	197	0.19	253	0.26

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
254	0.17	267	0.26	287	0.15	320	0.79
255	0.27	268	0.40	288	2.21	321	0.15
256	0.91	269	2.35	289	8.99	340	0.11
257	1.13	270	10.25	290	11.94	340	1.19
258	0.38	271	5.20	291	1.69	341	0.19
260	0.16	272	0.58	292	0.15	357	0.51
261	0.37	274	0.19	294	0.22	358	8.57
262	0.41	275	0.75	300	0.32	359	41.57
263	0.70	276	0.43	307	0.21	360	5.37
264	1.57	280	0.18	308	0.15	361	0.40
265	0.23	282	0.16	314	0.23		

13) 3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine

RMM 351 (15)

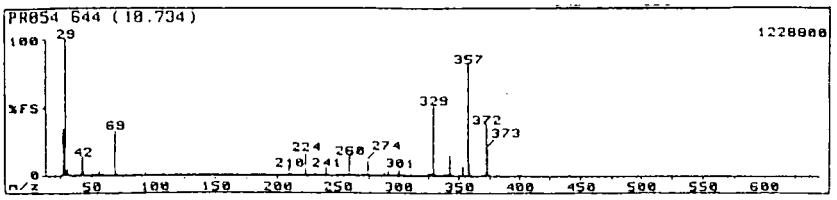


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.55	81	11.14	136	2.45	192	1.57
26	1.13	82	1.25	137	1.70	193	5.31
27	3.22	83	0.43	138	2.12	194	6.06
28	11.60	84	0.94	139	6.22	195	0.88
29	9.02	85	1.00	140	0.90	196	0.41
30	2.45	86	7.22	141	0.93	197	0.29
31	17.01	87	6.28	143	21.26	198	1.25
32	2.32	88	4.22	144	8.12	199	1.93
33	2.71	89	1.00	145	1.26	200	2.77
35	0.09	90	0.42	146	1.74	201	6.35
36	0.44	91	0.30	147	0.45	202	13.79
37	1.16	92	6.54	148	1.30	203	1.58
38	5.71	93	21.26	149	1.22	204	5.96
39	16.75	94	5.12	150	7.41	205	5.22
40	0.95	95	0.97	151	1.22	206	1.92
41	0.40	96	1.28	152	4.67	207	0.76
42	1.75	97	0.13	153	3.84	208	5.99
43	1.76	98	2.48	154	1.92	209	0.64
44	1.10	99	18.56	155	7.99	210	0.18
45	1.47	100	8.51	156	5.51	211	0.83
46	2.90	101	4.70	157	1.55	212	3.96
47	2.35	102	2.16	158	1.01	213	4.57
48	0.18	103	1.38	159	0.28	214	2.58
49	1.08	104	3.41	161	2.87	215	0.60
50	10.44	105	13.79	162	7.54	216	0.72
51	12.89	106	6.28	163	11.08	217	1.51
52	1.86	107	1.67	164	3.25	218	0.84
53	1.74	108	0.83	165	1.37	219	2.45
54	1.17	109	0.36	166	1.30	220	7.30
55	1.85	110	0.90	167	2.06	221	1.06
56	3.29	111	2.61	168	3.61	222	0.11
57	6.70	112	7.15	169	4.64	223	1.18
58	0.82	113	5.09	170	24.74	224	1.59
59	0.19	114	0.99	171	3.64	225	5.67
60	1.27	115	0.64	172	0.30	226	0.77
61	1.38	116	0.95	173	0.56	227	0.19
62	1.77	117	9.15	174	3.75	228	0.48
63	6.86	118	2.01	175	6.86	229	0.21
64	5.35	119	1.48	176	1.52	230	3.16
65	2.67	120	2.02	177	0.47	231	1.68
66	2.13	121	0.44	178	0.29	232	4.32
67	1.10	123	12.24	179	0.61	233	1.74
69	100.00	124	12.50	180	1.82	234	2.90
70	5.80	125	17.14	181	5.06	235	1.10
71	2.77	126	2.55	182	5.25	236	0.37
72	0.37	127	0.38	183	5.70	237	0.65
73	0.89	128	0.19	184	7.80	238	2.64
74	17.01	129	0.56	185	2.87	239	20.23
75	18.17	130	4.03	186	1.34	240	2.22
76	6.38	131	3.03	187	1.96	241	0.20
77	1.98	132	3.13	188	11.71	242	0.41
78	0.96	133	0.98	189	25.52	243	2.38
79	2.80	134	0.93	190	2.43	244	0.55
80	11.71	135	1.80	191	0.27	245	0.11

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
246	0.15	269	0.19	291	0.11	317	10.82
247	0.39	270	0.62	292	0.17	318	1.23
248	2.64	271	0.41	293	0.47	319	0.15
249	1.03	272	0.11	294	0.30	320	0.49
250	1.06	273	0.12	295	0.09	321	4.12
251	1.30	274	0.06	296	0.06	322	7.83
252	13.14	275	0.09	297	0.09	323	0.87
253	12.37	276	0.14	298	0.43	324	0.06
254	7.02	277	0.07	299	0.12	325	0.02
255	0.35	278	0.05	300	0.14	330	0.08
256	0.36	279	0.12	301	0.09	332	1.25
258	15.34	280	0.48	302	0.44	333	0.30
259	1.49	281	4.06	303	0.24	334	0.16
260	0.18	282	3.25	304	0.83	336	5.15
261	0.25	283	0.51	305	0.11	337	0.74
262	2.09	284	0.28	306	0.09	338	0.08
263	11.21	285	0.08	308	16.42	348	0.14
264	1.32	286	0.25	309	1.30	350	14.62
265	0.24	287	0.06	310	0.14	351	40.72
266	0.35	288	0.35	312	0.19	352	5.28
267	2.58	289	0.31	313	0.07	353	0.43
268	0.57	290	0.11	316	0.12		

14) diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine

RMM 372 (18)

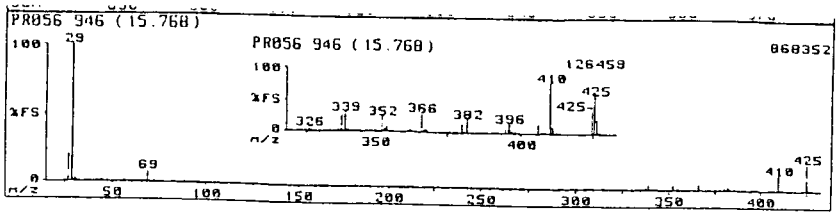


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.26	81	0.89	143	0.39	202	0.14
24	0.25	82	0.84	144	0.62	203	0.68
25	0.86	83	0.13	145	0.20	204	0.58
26	7.50	84	0.11	146	0.24	205	1.05
27	14.67	85	0.34	147	0.15	206	0.46
28	20.33	86	0.46	148	0.20	207	0.42
29	100.00	87	0.29	149	0.10	208	0.25
30	3.58	88	0.25	150	0.33	209	0.82
31	6.17	89	0.14	151	0.31	210	5.83
32	0.61	90	0.15	152	0.30	211	0.46
33	0.60	91	0.22	153	0.10	212	1.52
35	0.08	93	2.58	154	0.26	213	0.93
36	0.20	94	0.47	155	0.94	214	0.29
37	0.40	95	0.23	156	0.15	215	0.13
38	0.93	96	0.18	157	0.11	216	0.08
39	1.85	97	0.10	158	0.22	217	0.20
40	1.63	98	0.29	159	0.24	218	0.07
41	4.23	99	0.86	160	1.20	219	0.21
42	13.17	100	1.33	162	1.94	220	1.05
43	2.54	101	0.46	163	0.57	221	0.51
44	3.44	102	0.19	164	0.59	222	0.90
45	0.48	103	0.09	165	0.12	223	0.42
46	0.81	105	0.65	167	0.11	224	5.58
47	0.56	106	0.48	168	0.17	225	0.62
48	0.06	107	0.26	169	0.55	226	0.13
49	0.09	108	0.19	170	0.79	227	0.60
50	1.77	109	0.09	171	0.25	228	0.40
51	1.54	110	0.07	172	0.26	229	0.39
52	0.48	112	0.63	173	0.13	230	0.94
53	0.39	113	0.81	174	0.88	231	0.94
54	1.46	114	0.44	175	0.29	232	1.48
55	1.44	115	0.11	176	0.25	233	0.68
56	4.13	117	1.94	177	0.49	234	0.26
57	0.62	118	0.10	178	0.18	235	0.26
58	0.41	119	0.44	179	0.09	236	0.25
59	0.18	120	0.54	181	2.31	237	0.11
60	0.08	121	0.21	182	2.13	238	0.23
61	0.07	122	0.04	183	0.50	239	0.48
62	0.40	124	1.28	184	0.11	240	0.39
63	0.29	125	0.26	185	0.41	241	6.17
64	0.30	126	0.23	186	0.43	242	0.66
65	0.08	127	0.40	187	0.23	243	0.67
66	0.16	128	0.20	188	0.64	244	0.25
67	0.14	129	0.11	189	0.28	245	0.17
69	32.67	131	1.33	190	0.32	246	0.62
70	1.58	132	0.84	191	0.22	247	0.33
71	0.21	133	0.30	193	0.60	248	0.83
72	0.89	134	0.15	194	0.43	249	0.09
74	0.73	136	0.33	195	0.26	250	1.38
75	0.85	137	0.45	196	0.13	251	0.48
76	0.46	138	0.24	197	0.55	252	0.12
77	0.17	139	0.13	198	0.16	253	0.70
78	0.13	140	0.14	200	1.44	254	0.67
79	0.19	141	0.34	201	0.15	255	1.81

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
256	0.59	288	3.15	320	0.13	354	1.14
257	0.19	289	0.79	321	0.06	355	0.45
258	0.33	290	0.34	322	0.13	357	92.00
259	0.72	291	1.60	323	0.94	358	9.33
260	14.58	292	0.39	324	0.49	359	0.54
261	1.42	293	0.06	325	3.04	361	0.05
262	0.80	294	0.04	326	0.35	365	0.05
263	0.58	295	0.03	327	2.90	367	0.08
264	0.20	296	0.36	328	2.31	368	0.02
265	0.13	297	1.54	329	51.67	369	0.10
266	0.15	298	0.38	330	5.08	370	0.27
267	0.16	299	0.09	331	0.35	371	3.06
268	0.08	300	1.79	332	0.14	372	17.67
269	1.71	301	5.50	333	0.39	373	20.75
270	0.41	302	0.84	334	0.38	374	2.35
271	0.27	303	1.48	335	0.54	375	0.17
272	1.96	304	0.45	336	0.11	379	0.04
273	0.77	305	1.13	337	0.33	380	0.01
274	10.67	306	0.17	338	1.71	381	0.05
275	1.29	307	0.05	339	0.45	382	0.06
276	0.18	308	0.10	340	0.13	383	0.05
277	0.27	309	0.78	341	3.04	387	0.02
278	0.12	310	1.88	342	0.99	393	0.04
279	0.18	311	0.49	343	15.67	397	0.06
280	0.05	312	0.08	344	2.33	399	0.13
281	0.39	313	0.07	345	0.33	401	0.36
282	0.66	314	0.33	346	0.05	402	0.15
283	0.99	315	1.16	349	0.05	441	0.09
284	0.47	316	0.42	350	0.19	442	0.01
285	0.24	317	0.77	351	0.30	553	0.02
286	0.11	318	0.11	352	0.49	638	0.04
287	0.10	319	1.06	353	7.53		

15) {6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}diethylamine

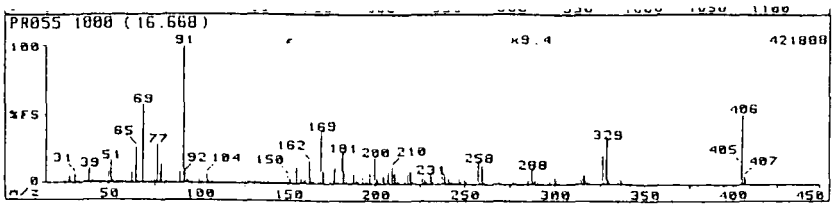
RMM 425 (19)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.08	81	0.13	142	0.04	206	0.08
24	0.09	84	0.06	143	0.07	207	0.12
25	0.11	85	0.07	144	0.23	209	0.11
26	2.99	86	0.13	145	0.13	210	0.13
27	20.75	87	0.03	146	0.09	211	0.04
28	8.37	88	0.09	147	0.05	212	0.07
29	100.00	89	0.06	149	0.05	213	0.11
30	2.77	90	0.04	150	0.12	214	0.13
31	1.16	91	0.04	151	0.12	215	0.09
32	0.13	93	0.37	152	0.11	216	0.12
33	0.11	94	0.13	153	0.05	219	0.17
35	0.07	95	0.09	155	0.18	220	0.06
36	0.05	96	0.09	156	0.08	221	0.13
37	0.14	97	0.04	157	0.11	222	0.07
38	0.31	99	0.15	158	0.14	223	0.10
39	0.66	100	0.52	159	0.11	224	0.04
40	0.42	101	0.18	160	0.04	225	0.09
41	0.52	102	0.13	161	0.05	227	0.09
42	1.65	103	0.02	162	0.17	228	0.28
43	0.73	105	0.05	163	0.11	229	0.21
44	2.86	106	0.10	164	0.11	230	0.12
45	0.11	107	0.07	165	0.13	231	0.08
46	0.09	108	0.06	166	0.07	232	0.07
47	0.23	109	0.06	167	0.12	233	0.29
48	0.04	110	0.04	168	0.11	234	0.06
50	0.52	112	0.06	169	0.17	235	0.13
51	0.59	113	0.13	170	0.08	236	0.22
52	0.16	114	0.16	171	0.12	237	0.08
53	0.24	115	0.08	172	0.14	238	0.11
54	0.74	116	0.08	173	0.06	239	0.06
55	0.66	117	0.12	174	0.11	240	0.23
56	1.18	118	0.03	175	0.11	241	0.44
57	0.42	119	0.11	176	0.11	242	0.40
58	0.13	120	0.08	177	0.06	243	0.40
59	0.13	121	0.06	178	0.08	244	0.05
60	0.06	122	0.05	179	0.07	245	0.10
61	0.06	123	0.05	181	0.13	247	0.09
62	0.09	124	0.16	182	0.13	248	0.05
63	0.09	125	0.08	183	0.15	249	0.07
64	0.12	126	0.05	185	0.16	250	0.43
65	0.06	127	0.25	186	0.07	251	0.21
66	0.11	128	0.09	188	0.13	252	0.08
67	0.06	129	0.08	189	0.05	253	0.09
69	8.61	130	0.08	190	0.36	254	0.22
70	1.02	131	0.14	192	0.12	255	0.22
72	1.10	132	0.10	194	0.17	256	0.25
73	0.12	133	0.06	196	0.13	257	0.40
74	0.19	134	0.04	197	0.19	258	0.07
75	0.37	136	0.10	200	0.13	259	0.30
76	0.22	137	0.12	201	0.06	260	0.05
77	0.07	138	0.08	202	0.15	262	0.08
79	0.12	139	0.06	203	0.04	263	0.35
81	0.29	140	0.09	204	0.13	264	0.14
82	0.23	141	0.11	205	0.11	265	0.23

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
266	0.14	305	0.20	338	3.61	377	0.14
267	0.06	306	0.19	339	4.33	378	0.13
268	0.06	307	0.13	340	0.68	380	2.03
269	1.21	308	0.25	341	0.32	381	0.32
270	0.47	309	0.08	342	0.19	382	3.21
271	0.14	310	0.20	343	0.04	383	0.33
272	0.06	311	1.10	344	0.14	385	0.08
273	0.11	312	0.19	346	0.13	386	0.05
275	0.03	313	0.18	347	0.14	387	0.02
277	0.13	314	0.15	348	0.41	388	0.13
278	0.33	315	0.05	349	0.08	390	0.22
279	0.18	316	0.04	350	0.52	391	0.07
280	0.12	317	0.03	352	1.43	392	0.06
281	0.15	318	0.04	353	0.94	395	0.91
282	0.12	319	0.19	354	1.33	396	1.35
283	1.12	320	0.33	355	0.20	396	3.21
284	0.18	321	0.11	356	0.17	397	0.52
285	0.41	322	0.24	358	0.07	398	0.10
286	0.06	323	0.12	360	0.43	404	0.08
288	0.07	324	0.13	361	0.21	406	2.03
291	0.12	325	0.71	362	0.81	407	0.32
292	0.27	326	0.93	363	0.10	408	0.12
293	0.14	327	0.21	364	0.30	410	11.33
294	0.13	328	0.22	366	4.39	411	1.42
296	0.12	330	0.06	367	1.05	412	0.11
297	0.61	332	0.61	368	0.85	424	0.43
298	0.41	333	0.20	370	0.10	425	5.17
299	0.08	334	0.66	372	0.10	425	9.71
300	0.24	335	0.20	374	0.05	426	1.30
301	0.05	336	0.14	375	0.03	427	0.42
304	0.05	337	0.16	376	0.60	428	0.04

16) benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine RMM 406 (20)

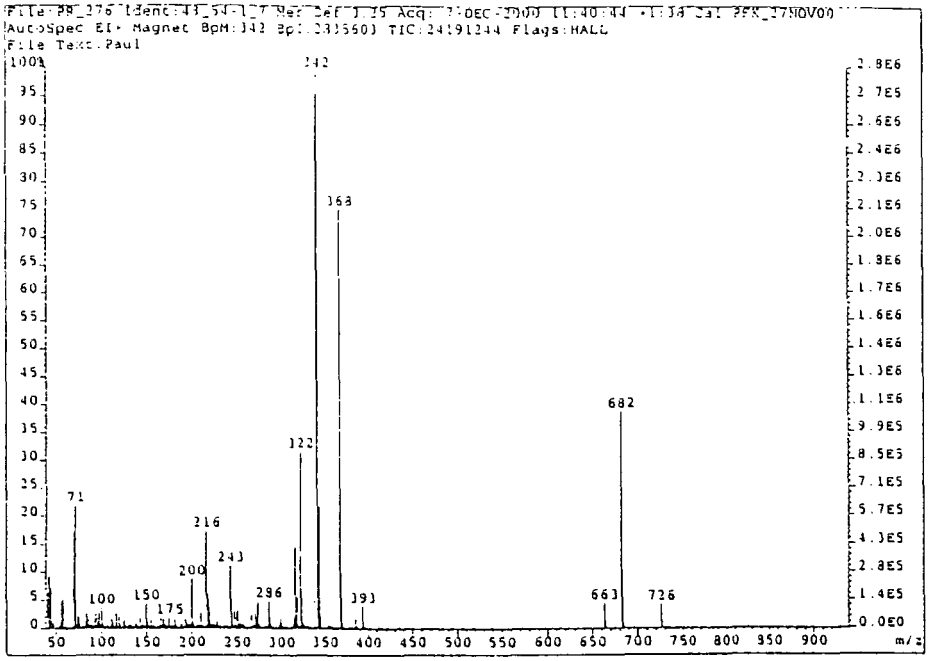


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.10	83	0.23	150	0.61	219	0.72
24	0.15	86	1.02	151	0.18	241	0.33
25	0.15	87	0.53	152	0.13	243	0.11
26	1.84	89	7.58	155	1.29	245	0.95
27	2.47	91	100.00	156	0.11	246	0.12
28	4.43	92	7.10	157	0.12	247	0.45
29	0.34	93	2.84	158	0.45	248	0.06
31	6.49	94	0.48	159	0.21	250	0.34
32	0.14	95	0.21	160	0.27	251	0.17
33	0.19	96	0.24	162	1.74	258	1.62
35	0.18	98	0.28	163	0.17	259	0.15
36	0.26	100	1.12	164	0.23	260	1.50
37	1.02	101	0.69	165	0.11	262	0.12
38	2.50	102	0.29	167	0.21	266	0.10
39	10.62	104	6.61	169	4.00	269	0.22
40	0.88	105	1.61	170	1.02	270	0.15
41	2.12	106	1.02	171	0.12	277	0.17
42	0.11	107	0.32	174	0.23	278	0.11
43	0.14	108	0.21	176	0.19	284	0.10
44	0.12	109	0.27	177	1.23	285	0.14
45	0.20	110	0.08	178	0.08	286	0.10
46	0.54	112	0.53	181	2.43	288	1.18
47	0.17	113	0.39	182	0.94	289	0.33
48	0.15	114	0.33	183	0.16	291	0.15
50	9.77	116	0.99	186	0.28	297	0.17
51	15.75	117	1.77	188	0.71	300	0.49
52	1.32	118	0.20	189	0.21	301	0.44
53	1.00	119	0.46	190	0.18	315	0.40
55	0.69	120	0.42	193	0.53	316	0.74
56	0.24	121	0.12	194	0.09	317	0.54
57	0.36	124	1.56	195	0.17	318	0.10
58	0.21	125	0.28	197	0.81	327	2.17
59	0.14	126	0.16	200	2.08	329	3.44
61	0.45	127	0.49	201	0.40	330	0.27
62	1.08	128	0.20	205	0.63	334	0.07
63	7.28	129	0.10	206	0.04	335	0.15
63	26.46	131	1.56	207	0.39	336	0.19
66	1.18	132	0.64	208	0.95	337	0.18
67	0.12	133	0.18	210	1.33	355	0.14
69	57.28	134	0.10	212	0.83	367	0.09
70	0.79	136	0.45	213	0.26	368	0.15
71	0.09	137	0.25	217	0.19	385	0.10
72	0.14	138	0.23	219	0.86	386	0.10
74	1.61	139	0.14	220	1.02	387	0.12
75	2.50	141	0.13	221	0.19	403	0.09
77	29.40	143	0.65	227	0.42	405	1.59
78	7.55	144	0.31	228	0.15	406	5.52
79	13.53	145	0.16	231	0.73	407	0.59
80	0.94	146	0.37	232	0.49		
81	0.93	147	0.15	236	0.10		
82	0.69	148	0.15	238	0.64		

17) 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene

RMM 682

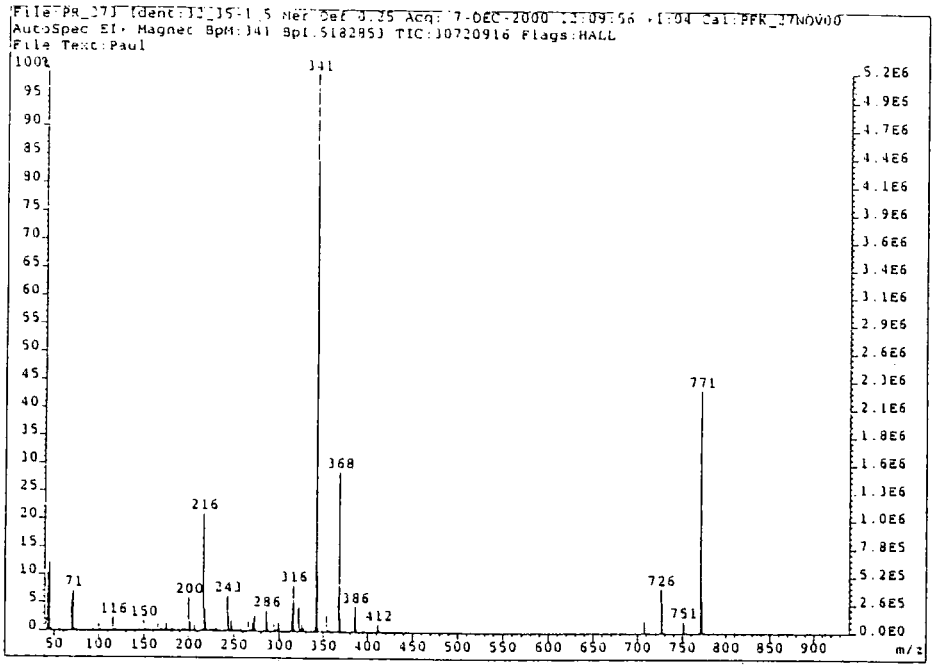
(35)



18) 25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene

RMM 770

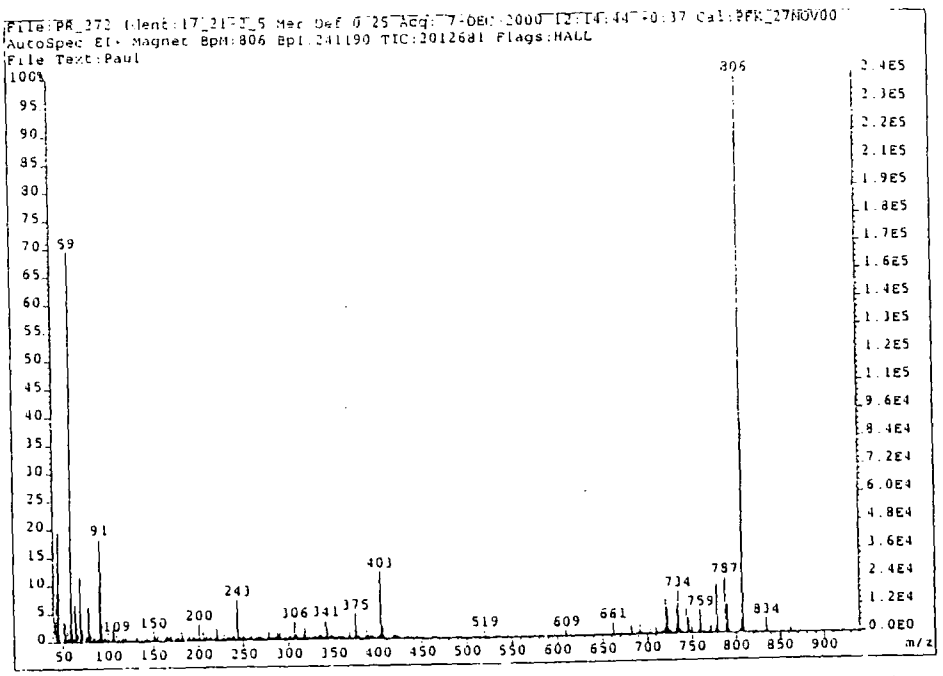
(37)



ABS MASS	REL INT HEIGHT	ABS MASS	REL INT HEIGHT	ABS MASS	REL INT HEIGHT	ABS MASS	REL INT HEIGHT
30.9966	1.18	187.9560	0.45	266.8401	0.33	340.9802	100.00
41.9973	0.79	188.9750	0.39	267.8977	0.57	341.9721	84.13
42.9944	14.43	192.9915	0.70	268.8249	0.40	342.9984	10.17
43.9852	1.11	197.9826	0.49	269.8710	1.29	343.9586	0.85
44.9885	12.35	199.9859	0.53	270.9018	1.58	347.4478	0.34
46.9745	0.57	198.8687	0.46	271.8861	0.64	353.8648	1.04
51.9782	0.30	199.8834	6.07	272.9083	2.91	354.8484	0.36
68.9970	5.62	230.8654	0.74	273.8881	0.39	355.8296	0.50
68.9689	1.77	291.8935	1.71	291.8639	1.53	363.8777	6.97
70.9965	7.32	304.8878	0.31	286.8155	1.83	366.7193	0.46
71.9825	0.38	305.9496	1.04	289.9008	1.83	367.4948	28.81
72.9652	0.47	304.9425	0.36	288.6741	1.63	368.9552	2.69
93.9109	0.47	313.8626	0.56	287.8212	0.38	383.9261	2.51
99.9142	1.34	314.8624	0.31	293.8983	1.48	384.9753	2.74
118.9930	0.31	315.9252	21.15	294.8196	0.35	385.9495	4.52
119.9944	2.49	316.9333	1.86	295.8143	0.41	386.9533	0.96
118.9134	0.32	317.9004	4.33	296.8454	0.31	409.9009	1.46
118.9101	0.65	318.8710	1.65	297.8447	0.32	411.9275	1.56
123.4845	0.32	321.8669	0.48	298.8746	1.86	429.8947	0.38
130.8660	0.67	324.4745	0.55	299.8597	1.30	768.5361	0.74
137.8818	0.35	327.8964	1.14	311.8706	1.18	708.3828	3.22
142.8695	0.47	329.8526	0.46	312.9130	4.49	707.3884	1.63
149.8648	1.36	330.8787	0.64	313.8931	2.12	735.3289	2.79
150.8900	0.32	338.8478	0.32	314.8801	1.36	736.3934	0.32
151.8830	0.32	342.8708	4.43	315.8789	0.43	736.3291	5.50
154.9689	0.53	343.9140	2.35	316.8671	0.75	750.3525	3.96
161.8969	0.72	344.8911	0.59	351.8998	1.56	751.8117	2.23
162.8762	0.36	346.8991	3.09	352.4077	1.14	752.8212	1.43
165.9160	1.31	347.8580	2.51	323.5447	0.41	768.3484	0.32
167.8916	0.40	348.8337	0.24	324.8525	0.75	769.5503	11.50
168.8881	0.58	352.8678	0.37	325.8735	1.42	770.3457	38.19
173.8762	0.34	353.8678	0.45	326.8565	0.51	771.1265	61.50
174.8640	1.43	355.8539	0.31	327.8486	0.76	772.4469	5.83
180.8782	0.70	356.8651	0.63	330.7937	1.02		
181.8660	0.42	365.8939	2.01	339.8091	1.02		

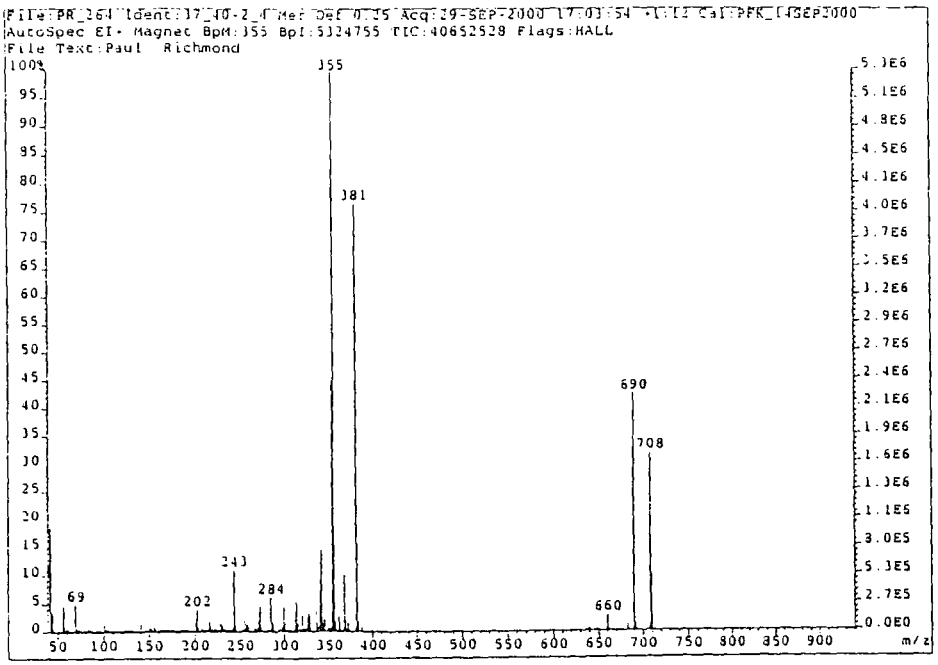
19) 26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene

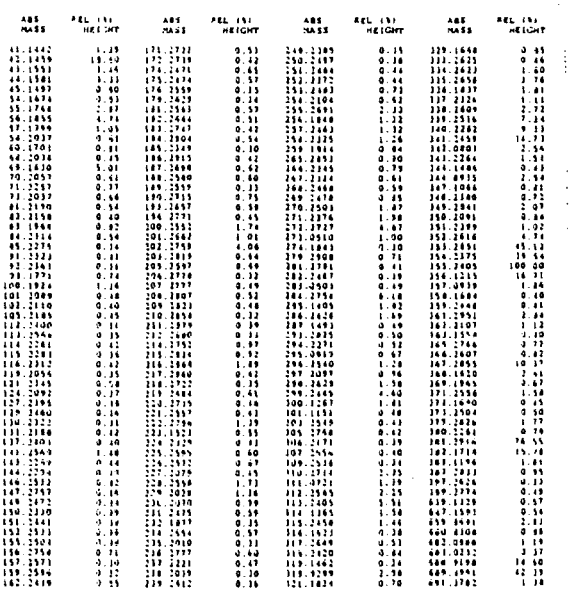
RMM 806 (39)



20) 11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20),15,17-hexaene

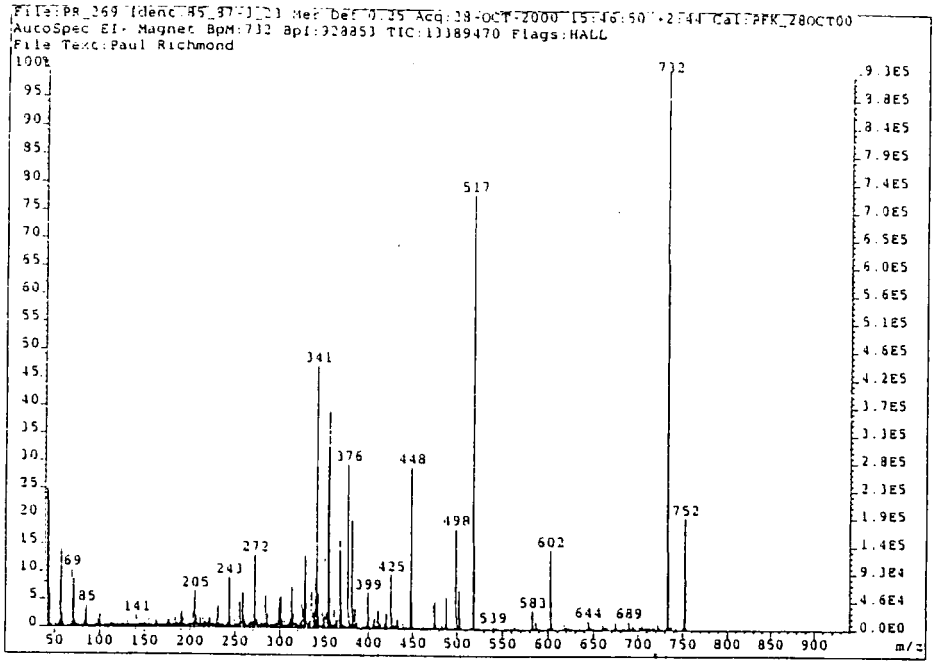
RMM 708 (42)

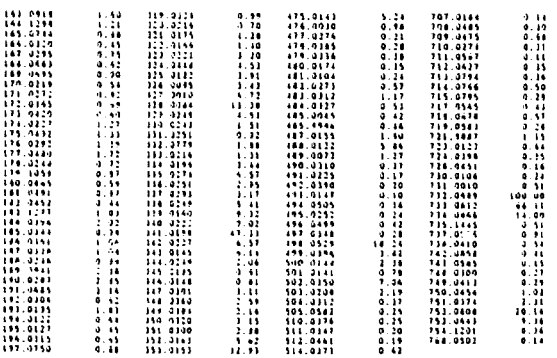




21) 2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene

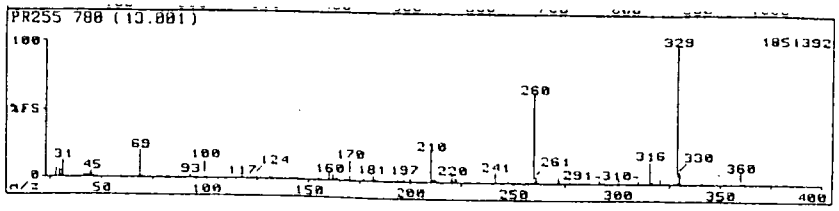
RMM 752 (43)





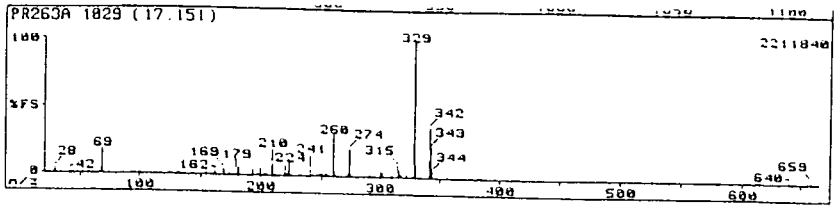
22) 2-({5,6-difluoro-3-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}amino)ethan-1-ol

RMM 360 (44a)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
27	3.07	111	3.20	194	1.09	272	4.31
28	7.08	122	1.13	197	4.87	289	1.36
29	5.37	141	1.33	200	2.45	291	2.53
30	4.65	143	1.02	205	1.60	300	1.45
31	12.50	144	1.33	210	22.35	301	3.01
41	2.42	155	2.17	211	1.87	310	3.29
42	2.59	160	4.70	212	2.20	316	17.26
43	3.44	162	4.09	220	4.87	317	1.67
44	4.20	163	1.06	222	2.77	321	4.09
45	4.42	164	1.71	227	1.05	329	100.00
46	1.16	169	2.13	232	1.26	330	8.90
69	20.58	170	3.65	233	1.20	341	1.78
70	1.22	177	1.66	241	8.19	360	8.66
93	2.74	181	4.59	247	1.65	361	1.09
100	2.18	182	3.54	250	1.18		
117	2.42	183	1.33	260	61.72		
124	2.21	193	1.41	261	5.31		

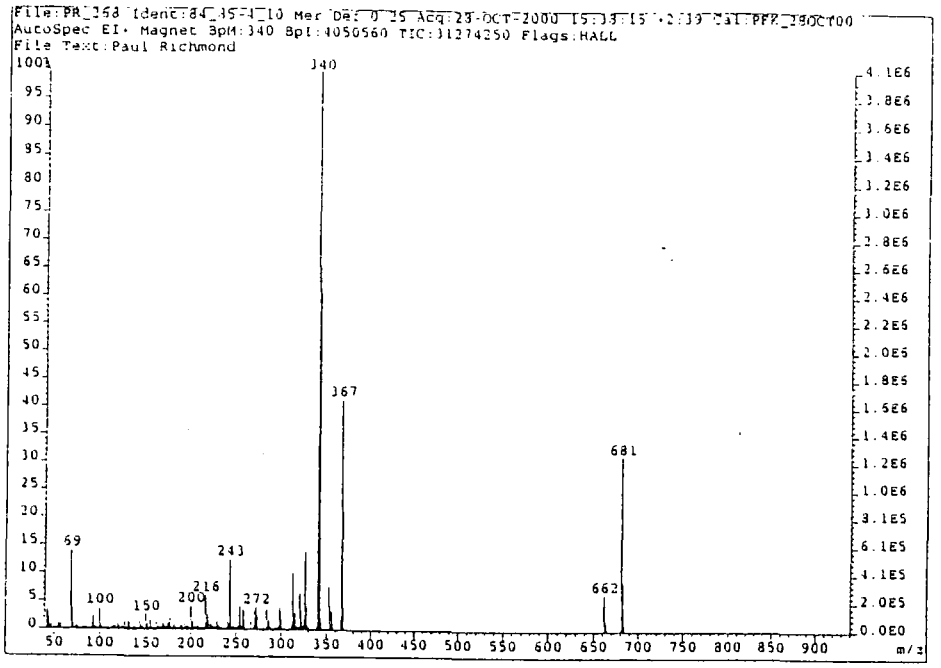
23) {3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyl)}(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}ethyl)amine RMM 659 (44)

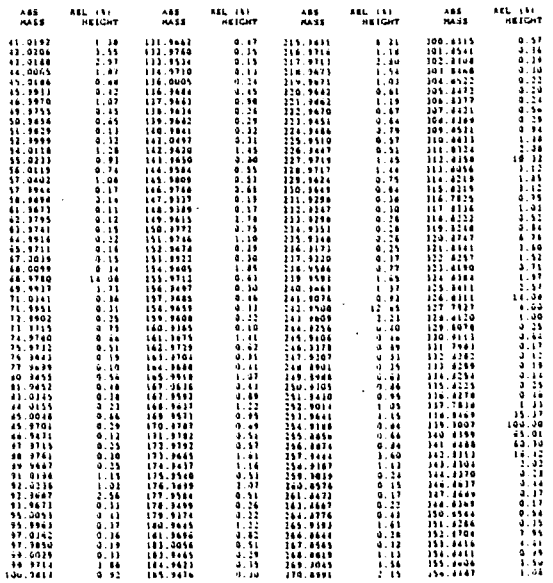


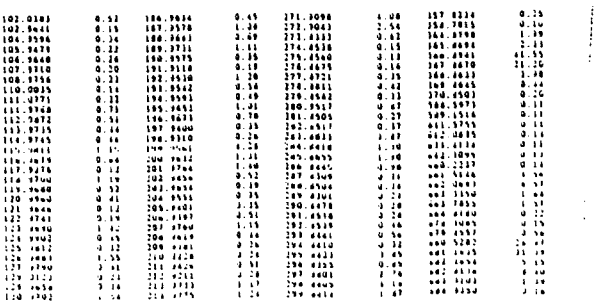
Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
27	1.33	182	3.96	238	1.31	301	2.95
28	3.80	183	1.19	241	5.28	302	3.61
42	2.23	188	1.46	243	1.67	312	2.72
69	18.15	193	5.14	246	2.48	315	8.33
93	1.64	197	2.12	248	1.53	316	4.54
100	1.88	198	1.96	249	1.64	317	2.49
117	1.26	200	5.46	250	2.95	318	2.05
124	1.50	203	1.56	253	1.91	323	3.19
131	1.78	205	1.96	254	1.55	327	1.33
132	1.05	210	9.17	255	2.35	329	100.00
150	1.01	212	2.36	260	30.93	330	10.14
155	1.68	219	1.46	261	2.80	341	13.52
160	1.52	220	7.64	272	4.81	342	37.79
162	2.95	221	1.34	273	1.49	343	22.96
169	4.40	222	2.74	274	20.00	344	5.14
170	1.98	224	10.09	275	2.41	448	1.10
174	1.98	225	1.01	288	1.19	640	2.34
177	1.19	231	1.44	289	1.03	659	3.06
179	11.85	232	1.24	291	1.98		
181	5.83	233	2.36	300	4.49		

24) 14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene

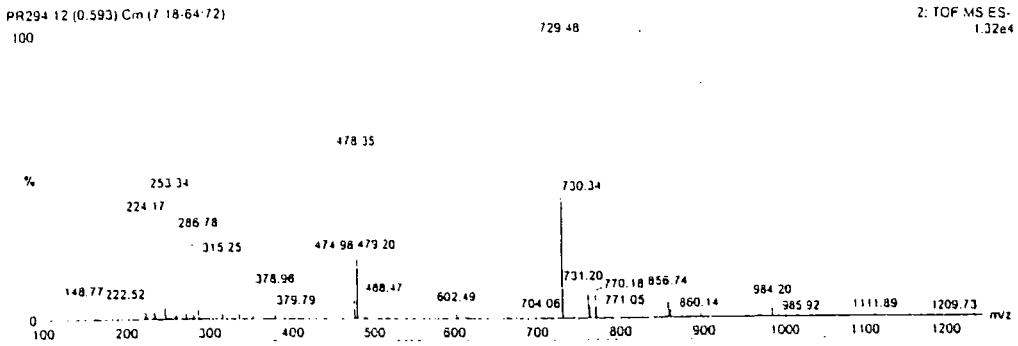
RMM 681 (45)



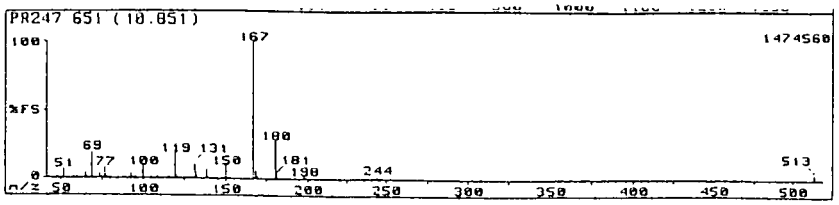




25) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine RMM 884 (46)

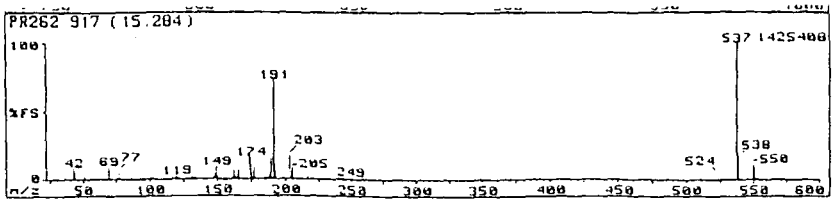


26) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane RMM 513 (47)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
47	1.70	89	1.32	120	1.77	168	5.61
51	6.32	93	4.03	127	1.23	169	1.89
57	1.01	95	2.12	131	10.31	180	28.03
59	1.42	100	9.17	132	4.06	181	2.45
65	4.31	105	1.51	138	6.53	198	2.24
69	19.44	108	1.23	139	1.27	244	2.73
74	3.14	109	1.84	148	1.11	513	3.53
75	1.37	113	1.35	150	9.31		
77	7.78	115	1.48	152	1.02		
78	1.58	119	13.39	167	100.00		

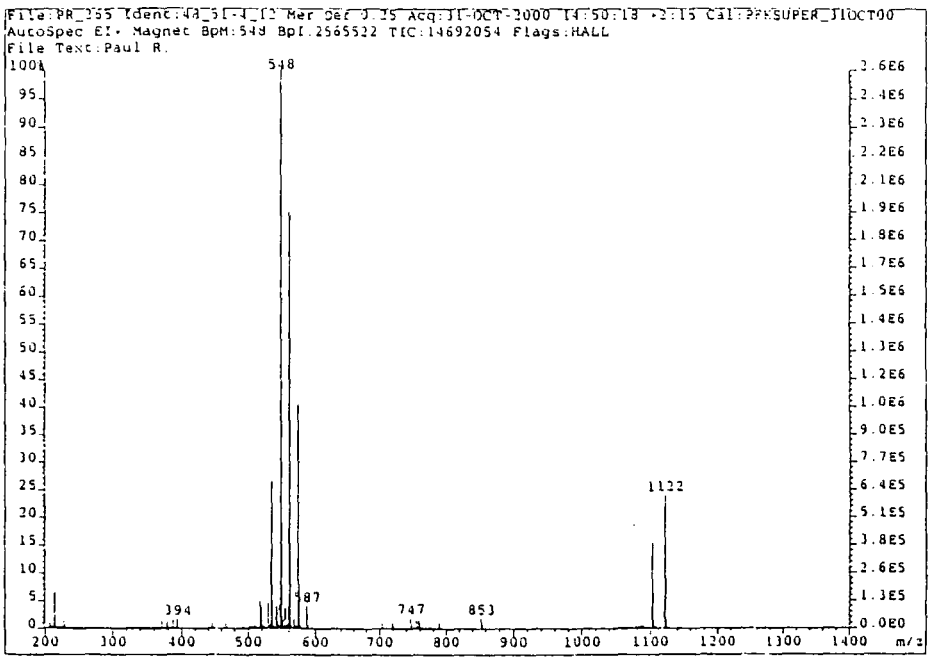
27) methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine RMM 1074 (48)



PR262 917 (15.284)

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
29	1.51	120	1.17	165	6.39	205	7.76
30	1.45	130	1.44	169	1.45	217	2.71
42	9.12	131	2.89	171	1.47	249	2.03
43	4.67	132	1.06	174	16.67	359	1.35
51	2.95	133	1.01	175	5.17	369	1.39
57	1.00	134	1.39	176	1.28	509	1.44
65	1.54	144	1.28	177	7.61	524	3.29
69	9.55	146	1.24	178	1.35	531	1.78
75	1.08	147	3.93	185	1.78	537	100.00
77	4.60	148	3.99	187	1.36	538	14.30
86	1.14	149	9.63	188	2.62	539	1.44
93	1.33	150	2.95	189	9.48	550	11.85
95	1.17	155	1.15	190	15.23	551	3.41
100	1.96	161	1.11	191	72.70	552	1.20
102	1.71	162	6.75	192	6.03		
116	1.65	163	5.39	203	17.10		
119	3.32	164	1.83	204	2.77		

28) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane RMM 1122 (49)

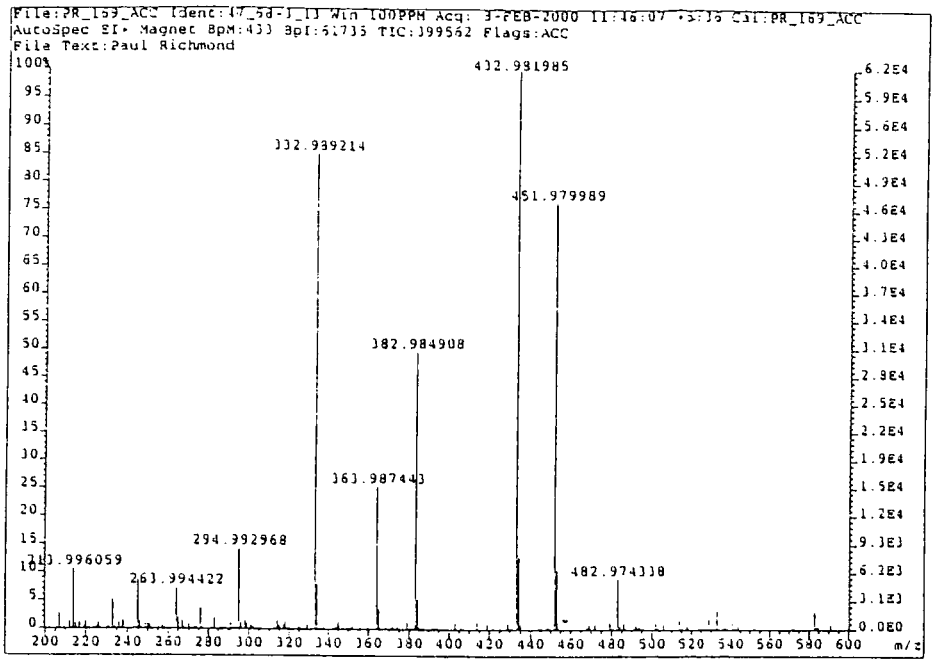


ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT
391.0832	0.46	444.1459	1.08	545.0706	1.94	747.1448	2.05
394.0927	0.32	447.1459	0.24	546.0778	0.63	748.1419	0.54
395.4463	0.31	447.5717	0.91	547.0626	2.59	755.1481	1.01
396.0916	0.49	455.4907	0.66	548.0711	100.00	756.1513	0.75
397.0557	1.18	498.0797	0.53	549.0712	19.28	759.1456	1.47
398.3912	1.22	500.0568	0.31	550.0653	2.65	760.1747	0.53
399.9771	0.35	501.0738	0.33	551.0900	1.41	774.8992	3.45
410.0939	0.34	504.0535	0.37	552.2081	1.31	789.0851	1.14
411.0944	0.47	505.3561	0.44	554.1041	2.84	790.1114	0.76
412.0765	1.56	506.0508	0.32	555.0916	0.44	853.1698	2.02
413.0840	0.44	510.0729	0.83	556.0966	1.04	854.1719	0.76
414.0752	6.75	512.0838	0.42	557.0988	1.28	904.0841	0.41
415.0642	2.33	515.0616	0.35	558.0854	1.25	951.1371	0.44
415.9464	0.36	516.0679	0.42	559.0666	0.68	1003.1263	0.76
420.0911	0.40	517.3737	1.59	560.0684	4.00	1074.0687	0.40
421.0789	3.43	518.0211	5.20	561.1410	73.35	1079.0816	0.41
422.0514	0.56	518.0318	1.16	562.0944	13.87	1083.0915	0.36
426.0668	0.60	520.0508	2.93	563.0847	1.55	1083.1095	0.67
427.0842	0.44	521.0561	1.65	564.0963	0.32	1084.1161	0.45
428.0967	1.56	522.0821	0.10	566.0743	3.41	1085.1539	0.47
429.0771	0.43	523.0815	0.16	567.0691	0.55	1086.1361	0.32
430.1100	0.88	524.2681	0.46	568.0560	1.42	1087.0957	0.76
436.1961	0.37	525.0860	0.16	569.1006	0.84	1088.0871	0.39
440.0943	0.65	526.0768	0.61	570.1053	0.69	1089.3854	0.41
442.1110	0.64	527.3616	0.39	573.0764	1.76	1095.9526	0.62
456.3026	0.35	528.3646	1.52	574.0797	0.93	1098.0165	0.33
457.1554	0.36	529.4681	0.53	574.0870	10.30	1101.0605	0.35
461.0546	0.34	530.0781	0.80	575.2669	0.77	1102.1038	1.35
492.0936	0.36	531.0737	0.69	576.0972	1.69	1103.1144	15.44
495.0796	0.30	532.2835	0.88	577.0963	0.37	1104.1338	1.66
498.1468	0.56	533.0597	0.78	582.1121	0.31	1105.1389	1.65
500.0651	0.54	534.2617	1.00	586.0878	1.16	1107.0687	0.67
503.1961	1.46	535.3608	26.78	587.0951	4.21	1108.1006	0.58
513.2953	0.46	536.4661	3.09	588.1002	2.02	1120.0848	0.61
519.1967	0.39	537.5192	2.86	589.1047	0.65	1121.1012	1.10
539.1421	1.24	538.0571	0.75	704.1314	1.12	1122.1131	24.14
540.1589	0.50	540.3637	0.67	705.1396	0.35	1123.1317	3.29
541.1545	0.42	541.0734	2.43	719.1438	1.24	1124.1292	1.82
542.2149	1.63	542.3926	4.27	720.1498	0.61	1125.1217	0.54
544.2284	1.76	543.1024	3.57	735.1417	0.33		
545.2146	0.13	544.0825	1.14	739.1491	0.49		

29) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine

RMM 452

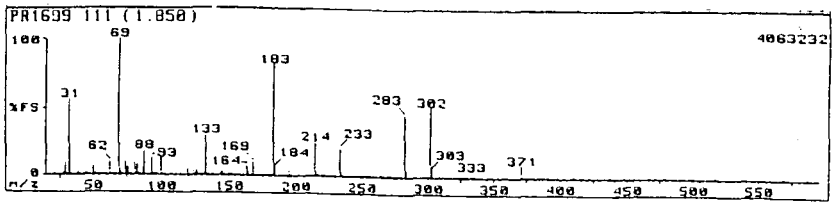
(50)



30) 2,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine

RMM 302

(51)

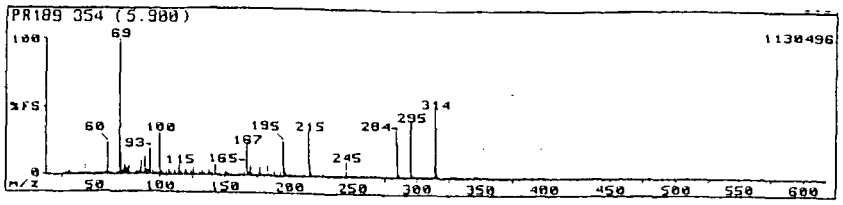


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	1.60	86	0.87	155	0.50	224	0.02
21	0.05	88	18.55	157	0.22	226	0.09
24	0.31	89	0.91	157	0.29	227	0.07
25	0.26	90	0.17	158	0.13	228	0.05
26	4.84	91	0.05	159	0.14	229	0.01
27	1.71	93	12.80	161	0.40	230	0.02
28	8.77	94	0.55	162	0.43	231	0.07
29	0.80	95	0.85	164	3.68	233	20.56
31	56.05	96	0.12	164	7.06	234	2.65
32	1.24	98	0.07	165	3.33	235	0.17
33	0.21	98	0.06	166	0.14	238	0.10
35	0.69	100	12.40	167	0.03	239	0.03
36	0.71	101	0.67	169	9.58	240	0.10
37	0.47	102	0.14	170	0.30	241	0.01
38	2.80	103	0.03	174	0.13	242	0.02
39	0.87	105	1.66	174	0.10	243	0.04
40	0.23	107	3.83	176	0.55	245	3.30
41	0.32	108	0.13	176	0.53	246	0.30
42	0.60	109	0.02	177	0.18	247	0.06
43	1.47	110	0.01	178	0.04	248	0.01
44	0.64	112	1.74	181	0.12	249	0.01
45	1.92	114	2.39	181	0.28	250	0.23
46	0.38	115	0.17	183	81.85	251	0.02
47	0.40	117	0.31	184	5.54	252	0.09
48	0.08	119	5.32	188	0.67	253	0.02
50	6.38	120	0.40	190	0.08	254	0.01
51	1.27	121	0.21	190	0.06	255	0.01
52	0.24	122	0.03	191	0.03	256	0.01
53	0.08	124	3.45	193	0.14	257	0.05
55	1.03	126	3.68	193	0.10	258	0.02
56	0.28	127	0.24	195	3.88	259	0.02
57	1.10	128	0.05	196	0.88	260	0.02
58	0.19	129	0.02	197	0.39	261	0.02
59	0.04	131	4.21	200	0.43	264	2.75
62	9.48	133	30.24	201	0.05	265	0.77
63	0.39	134	1.32	202	0.07	266	0.44
64	0.30	135	0.10	203	0.01	267	0.05
65	0.07	136	0.07	205	0.15	269	0.04
66	0.09	138	1.66	206	0.02	270	0.02
69	100.00	138	3.43	207	0.22	271	0.03
70	3.63	139	0.21	208	0.05	272	0.01
71	1.23	140	0.03	209	0.01	273	0.01
72	0.11	142	0.96	210	0.02	274	0.01
74	10.08	143	1.92	211	0.02	275	0.00
75	2.22	145	2.34	212	0.04	276	0.06
76	5.80	145	4.54	214	25.50	277	0.03
77	0.21	146	0.43	215	2.87	278	0.06
78	0.08	147	0.06	216	0.12	279	0.02
79	0.18	148	0.03	217	0.02	280	0.02
81	8.57	149	0.98	219	0.19	281	0.03
82	0.38	150	2.42	220	0.03	283	45.56
83	8.06	151	0.93	221	0.03	284	4.99
84	0.41	152	1.55	222	0.01	285	0.49
85	0.47	153	0.08	223	0.02	286	0.07

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
288	0.05	331	0.01	377	0.05	429	0.07
288	0.07	333	5.14	378	0.29	433	0.01
289	0.02	334	0.49	379	0.05	435	1.03
290	0.06	335	0.05	380	0.01	436	0.14
291	0.02	336	0.01	381	0.00	437	0.01
295	0.27	338	0.03	383	0.71	440	0.03
296	0.03	339	0.02	384	0.08	441	0.01
297	0.03	340	0.09	385	0.37	445	0.03
298	0.01	341	0.03	386	0.05	447	0.03
299	0.02	342	0.01	387	0.01	448	0.02
300	0.04	345	0.04	388	0.01	449	0.01
302	51.61	346	0.01	390	0.38	452	0.04
303	5.95	347	0.10	391	0.05	453	0.00
304	0.29	348	0.02	395	0.09	459	0.01
307	0.04	349	0.05	396	0.02	466	0.05
308	0.02	350	0.01	397	0.10	467	0.03
309	0.03	352	0.16	398	0.01	471	0.02
310	0.05	353	0.18	399	0.01	478	0.02
311	0.03	354	0.03	402	0.07	479	0.01
313	0.01	357	0.13	403	0.04	485	0.02
314	0.09	358	0.03	404	0.01	497	0.09
315	0.06	359	0.10	407	0.09	498	0.03
316	0.02	360	0.05	408	0.02	499	0.01
317	0.04	361	0.01	409	0.02	516	0.28
319	0.23	364	0.05	410	0.02	517	0.08
320	0.03	365	0.04	411	0.01	535	0.03
321	0.07	366	0.04	414	0.05	536	0.00
322	0.03	367	0.06	415	0.01	547	0.03
323	0.01	368	0.02	416	0.03	567	0.03
324	0.02	369	0.01	417	0.05	568	0.01
326	0.04	371	9.48	418	0.02	585	0.45
327	0.01	372	0.92	421	0.20	586	0.07
328	0.06	373	0.10	422	0.03	587	0.01
329	0.03	374	0.01	426	0.04		
330	0.01	376	0.36	428	0.05		

31) 2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine

RMM 314 (52)



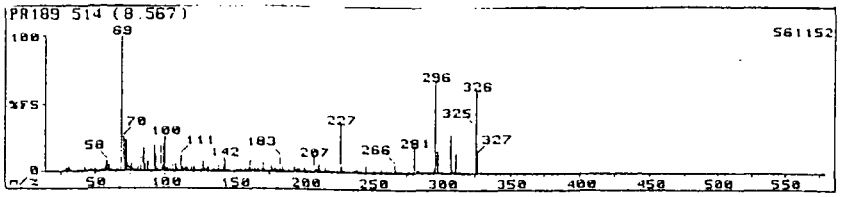
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	79	0.55	139	0.43	202	0.62
24	0.02	80	1.12	140	0.36	203	0.40
25	0.03	81	3.87	141	0.19	204	0.17
26	0.53	82	1.65	143	4.69	205	0.15
27	0.12	83	2.67	143	8.06	207	1.10
28	0.75	84	3.42	144	1.27	208	0.13
29	1.95	85	11.05	145	1.79	209	0.07
30	0.50	86	1.08	146	0.74	211	1.77
31	4.23	87	2.38	147	0.83	212	0.16
32	0.11	88	11.95	148	0.52	213	33.33
33	0.19	89	4.03	149	1.26	214	8.51
35	0.21	90	3.51	150	4.10	217	2.45
36	0.26	91	3.31	151	2.60	219	0.79
37	0.09	92	8.70	152	2.42	220	0.56
38	0.42	93	19.75	153	0.92	221	0.27
39	0.15	94	1.61	154	0.29	222	0.05
40	0.13	95	2.65	155	0.23	223	0.10
41	0.10	96	1.30	156	0.40	225	2.15
42	0.20	97	0.84	157	1.00	226	1.90
43	0.76	98	1.92	158	0.42	227	1.14
44	0.42	100	31.16	159	0.33	228	0.17
45	1.43	101	2.81	161	3.31	229	0.10
46	1.01	102	2.49	162	1.09	230	0.10
47	0.87	103	0.52	163	0.34	231	0.12
48	0.03	105	3.87	165	8.79	233	1.74
50	2.42	107	5.07	167	22.55	234	1.07
51	0.35	108	2.42	168	1.59	235	0.27
52	0.86	109	1.08	169	5.23	236	0.04
53	0.46	111	3.53	170	7.43	238	1.16
54	0.58	112	2.29	171	0.80	239	1.47
55	0.63	114	5.80	172	0.21	240	0.16
56	0.61	115	7.43	174	0.48	241	0.02
57	2.26	116	3.33	176	2.99	243	0.15
58	0.63	117	1.81	177	5.34	245	10.42
59	4.17	119	4.21	178	0.55	246	1.79
60	21.55	120	4.14	179	0.46	247	0.85
61	0.35	121	1.54	180	0.61	249	0.36
62	1.16	122	0.67	181	1.45	250	0.04
63	0.52	124	1.77	183	7.38	252	0.22
64	0.71	124	3.53	184	0.38	253	0.04
65	0.57	125	3.42	185	0.16	254	0.01
66	0.56	126	5.17	186	0.11	255	0.02
67	1.54	127	0.53	188	4.30	256	0.02
68	16.58	129	0.47	189	0.42	257	0.57
69	100.00	129	0.77	190	0.12	258	0.13
70	15.11	130	2.06	191	0.06	259	0.04
71	2.98	131	3.06	193	3.92	260	0.15
72	6.16	132	2.11	195	25.72	261	0.10
73	7.43	133	3.65	196	6.07	262	0.03
74	4.19	134	1.19	197	2.94	264	0.46
75	3.42	135	0.35	198	0.65	264	1.29
76	7.25	136	0.58	199	0.31	265	0.35
77	0.59	137	2.33	200	1.83	266	0.26
78	1.09	138	1.30	201	0.48	267	0.35

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
268	0.04	311	0.05	355	0.02	399	0.03
269	0.01	313	9.33	357	0.02	400	0.02
271	0.12	314	50.36	359	0.05	402	0.17
272	0.07	315	17.32	360	0.01	403	0.01
273	0.04	316	2.90	361	0.24	407	0.40
274	0.04	317	0.25	362	0.06	408	0.04
275	0.21	321	0.02	363	0.01	409	0.09
276	0.87	322	0.03	364	0.02	414	0.35
277	0.29	324	0.05	365	0.02	415	0.05
278	0.04	325	0.07	366	0.02	419	0.02
280	0.16	326	0.05	369	0.02	422	0.03
281	0.05	327	0.04	371	0.03	429	0.05
284	34.06	329	1.77	372	0.02	430	0.01
285	24.28	330	0.13	373	0.02	433	0.01
286	1.68	331	0.04	374	0.04	438	0.02
287	0.09	333	0.06	377	0.02	440	0.12
289	0.02	334	0.03	379	0.02	441	0.04
291	0.02	336	0.02	380	0.01	447	0.06
293	0.30	339	0.02	381	0.02	452	0.01
295	40.58	340	0.04	383	1.25	457	0.12
296	2.90	341	0.03	384	0.18	458	0.02
297	0.12	342	0.02	385	0.03	459	0.02
298	0.04	345	1.54	388	0.03	464	0.08
299	0.06	346	0.17	389	0.03	502	0.04
300	0.10	347	0.46	390	0.14	507	0.35
301	0.03	348	0.06	391	0.03	509	0.02
302	0.07	349	0.03	392	0.02	509	0.25
304	0.63	352	0.04	395	0.05	613	0.03
307	0.05	353	0.07	396	0.01		
309	0.03	354	0.05	397	0.02		

32) 5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine

RMM 326

(53)

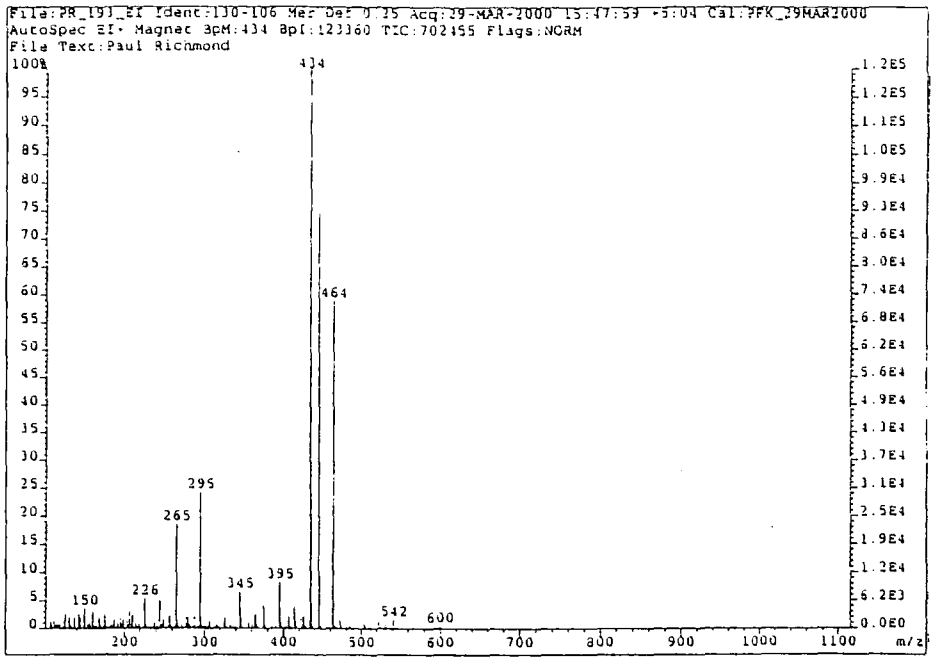


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.08	81	4.24	142	10.22	201	0.76
24	0.05	82	1.65	143	7.30	202	0.32
26	0.49	83	10.77	144	1.02	203	0.90
27	0.33	84	8.67	145	1.98	204	1.74
28	2.89	85	17.52	146	0.62	205	0.25
29	1.79	86	5.20	147	0.45	207	10.39
30	1.47	88	7.76	148	0.87	208	1.01
31	3.92	89	1.28	149	1.92	209	1.69
32	0.25	90	0.54	150	2.13	210	1.74
33	0.23	92	19.34	151	2.02	211	6.34
35	0.47	93	12.04	152	1.40	212	1.15
36	0.50	94	1.45	153	1.77	213	0.64
37	0.16	95	1.98	154	2.92	214	1.25
38	0.72	97	19.89	155	0.71	216	3.42
39	0.17	98	4.01	156	0.92	217	1.96
40	0.18	99	20.40	157	2.87	218	0.12
41	0.72	100	25.73	158	1.74	219	0.27
42	3.42	101	1.98	159	1.60	220	0.38
43	2.40	102	3.29	160	2.75	221	0.65
44	1.09	103	1.95	161	8.49	222	0.17
45	1.16	105	4.93	162	1.98	223	0.96
46	1.14	107	5.98	163	0.61	225	3.74
47	2.43	108	1.89	164	1.38	227	34.49
48	0.06	109	1.40	165	2.92	228	1.92
50	2.53	111	11.31	166	2.97	229	0.89
51	1.24	112	2.82	167	1.17	230	0.27
52	1.20	113	1.61	169	2.38	231	0.16
53	1.07	114	2.85	170	7.07	233	0.73
54	1.93	115	3.97	171	1.38	235	1.24
55	1.84	116	3.13	172	1.02	236	0.15
56	4.65	117	1.12	173	0.88	237	1.93
57	4.33	119	4.33	174	0.46	238	0.79
58	7.48	120	3.56	176	5.34	239	2.78
59	2.33	121	1.17	177	2.37	240	0.59
60	4.79	122	0.83	178	1.33	241	0.19
61	0.12	123	0.74	179	2.87	242	0.36
62	0.81	124	2.17	180	1.15	243	0.54
63	0.44	125	1.61	181	1.87	246	4.79
64	0.91	126	4.79	183	10.86	247	0.32
65	0.99	127	7.98	184	4.20	248	0.24
66	1.17	128	1.43	185	1.39	249	0.22
67	3.06	129	2.40	186	0.58	250	2.38
69	100.00	130	3.10	188	2.34	251	0.12
70	25.55	131	3.42	189	0.64	252	0.23
71	8.62	132	1.32	190	0.40	253	0.21
72	23.13	133	2.24	192	3.65	254	0.58
73	6.80	134	1.85	193	4.11	255	0.61
74	4.24	135	1.70	194	0.86	256	0.17
75	3.10	136	0.48	195	2.55	257	3.47
76	6.02	137	1.69	196	1.76	258	0.32
77	1.61	138	4.61	197	2.60	259	0.08
78	1.37	139	1.28	198	1.41	261	2.32
79	1.17	140	0.91	199	4.11	262	0.30
80	1.68	141	4.11	200	2.84	263	0.65

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
264	0.12	281	18.43	298	1.13	327	13.14
265	0.75	282	1.80	299	0.07	328	1.03
266	6.11	283	1.30	300	0.05	329	0.12
267	1.79	284	0.24	301	0.03	338	0.03
268	0.88	287	0.16	305	0.13	341	0.41
269	0.19	288	0.15	307	28.10	342	0.04
270	0.13	289	0.04	308	2.92	357	0.12
271	0.02	291	0.17	309	0.32	373	0.09
273	0.08	292	0.27	311	14.78	395	0.17
275	0.06	293	0.07	312	1.00	396	0.03
276	0.17	294	0.05	313	0.13	413	0.06
277	1.13	295	3.51	314	0.05	572	0.01
278	0.76	296	67.15	325	33.39		
279	0.17	297	15.42	326	60.53		

33) 6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine

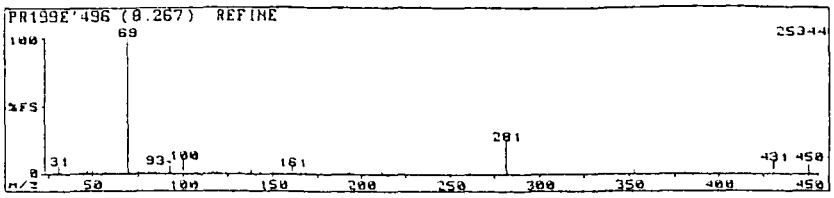
RMM 654 (54)



34) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine

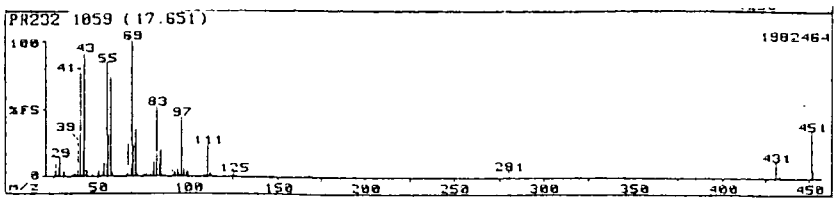
RMM 464

(55)



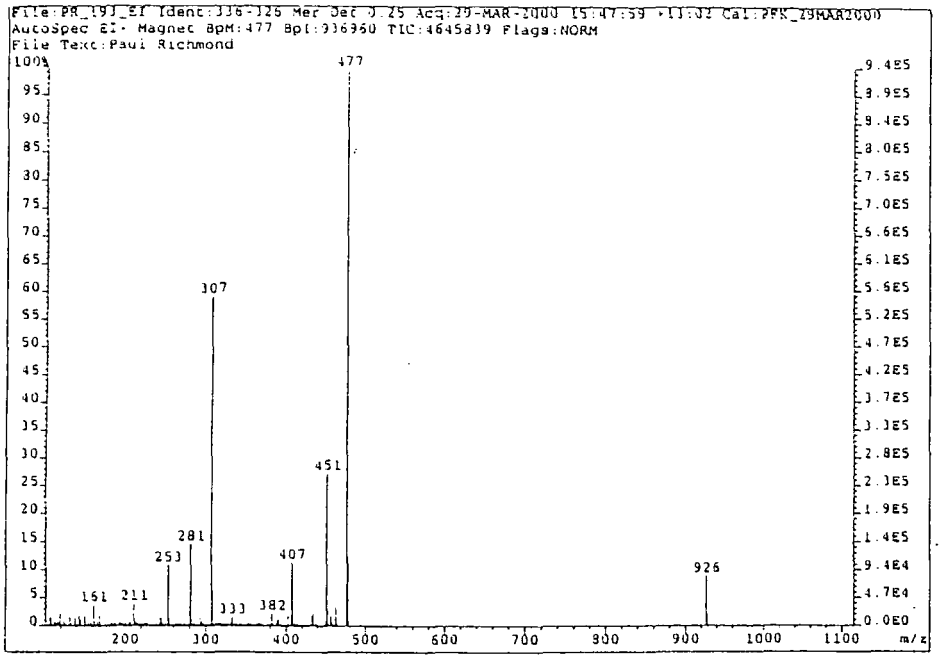
Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
28	0.62	81	1.61	138	1.87	223	2.08
29	1.67	83	1.33	141	1.25	243	2.41
31	6.19	84	2.10	150	2.11	261	1.89
32	0.82	92	5.05	154	1.70	281	24.43
43	1.59	93	6.06	161	5.18	282	2.46
45	1.29	100	9.28	162	2.07	316	1.42
46	1.63	105	1.03	166	2.24	331	1.59
47	1.27	107	1.93	169	1.48	353	3.61
50	2.43	108	1.64	188	1.45	381	1.59
57	1.96	116	1.53	192	1.77	431	8.59
69	100.00	117	0.82	193	2.57	432	1.23
70	2.98	119	2.04	200	1.82	450	3.71
74	1.64	124	2.02	211	3.35	451	1.24
76	2.27	131	2.34	212	1.23		

35) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine RMM 618 (56)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
26	3.51	53	13.13	81	10.95	112	2.71
27	9.56	54	10.41	82	9.56	113	1.28
28	6.04	55	81.47	83	51.86	125	2.25
29	13.34	56	29.75	84	10.07	125	2.74
31	1.51	57	72.71	85	19.42	138	1.01
35	1.14	58	3.20	86	1.18	161	1.14
36	1.92	65	3.16	91	4.65	165	1.03
37	1.94	66	1.71	92	1.07	166	1.38
38	3.93	67	24.38	93	3.41	167	1.51
39	25.41	68	7.02	95	5.79	168	1.14
41	76.86	69	100.00	96	2.20	281	4.44
42	19.42	70	22.73	97	43.39	413	1.34
43	90.91	71	34.50	98	5.42	431	11.67
44	4.49	72	1.70	99	3.51	432	1.23
47	2.41	74	1.15	100	3.72	433	1.59
50	3.93	76	1.87	109	2.18	451	35.12
51	4.49	77	2.52	109	1.18	452	5.71
52	1.34	79	5.06	111	23.76		

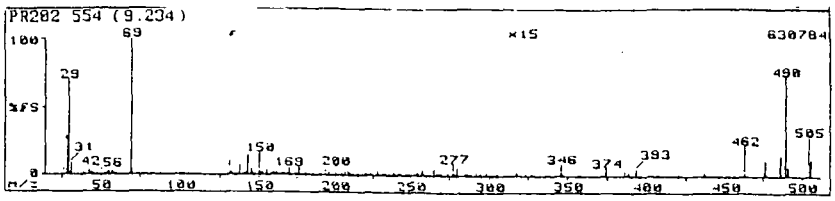
36) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine RMM 926 (57)



ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT
104.9791	0.41	186.0084	0.67	261.0181	14.66	390.0358	1.26
104.9830	1.79	208.0024	0.72	262.0057	1.67	391.0269	0.29
107.9924	0.48	304.0000	1.30	281.0284	0.65	402.0287	1.99
111.0133	0.35	305.0028	0.61	285.0380	0.57	406.0529	1.74
114.9883	0.79	307.0058	0.74	286.0077	0.62	407.0645	11.84
113.9901	0.92	311.0042	4.05	291.0122	0.33	408.0630	1.17
115.9860	0.36	313.0101	3.98	291.0142	1.39	409.0552	0.32
116.9886	0.60	313.0108	0.46	294.0033	0.79	411.0110	0.49
118.9861	2.38	314.0077	0.19	295.0301	0.93	414.0211	0.38
123.9896	0.83	315.0092	0.71	297.0252	0.43	422.0106	0.48
125.9956	0.17	319.0036	9.38	305.0054	0.54	430.0132	0.48
127.9864	0.31	323.0009	0.68	306.0157	0.46	431.0546	1.82
130.9869	1.65	324.0191	0.37	307.0176	58.03	432.0586	0.31
131.0027	0.64	325.0284	0.61	308.0447	6.54	433.0317	1.76
137.9914	1.49	328.0152	0.39	309.0494	0.65	434.0451	2.17
141.9938	0.32	329.0071	0.50	311.0322	0.36	435.0494	0.36
142.9888	1.98	331.0045	0.47	313.0300	0.54	437.0689	0.63
144.9979	1.11	338.0219	0.44	314.0186	0.71	438.0601	0.24
149.9908	1.79	339.0267	0.35	318.0364	0.40	439.0687	0.66
150.9911	0.61	341.0034	0.65	319.0344	0.51	444.1605	0.31
153.9969	0.82	343.0089	1.44	323.0210	0.35	448.0758	1.15
154.9967	0.44	344.0086	0.32	325.0491	0.50	449.0876	0.54
156.9976	0.87	345.0135	1.38	331.0093	0.71	450.0539	4.58
158.0001	0.51	350.0252	3.56	333.0300	1.57	451.0656	27.38
160.9931	3.66	351.0315	100.00	337.0645	0.40	452.0702	3.20
161.9960	0.86	354.0334	1.33	339.0835	0.33	456.0749	0.41
164.0043	3.37	355.0391	0.33	341.0301	0.69	457.0617	1.71
165.9960	0.82	357.0114	0.37	351.0485	0.33	458.0784	0.53
168.9942	0.32	361.0148	0.59	352.0509	1.35	463.0640	3.40
168.9967	1.98	363.0316	0.33	362.0433	0.56	464.0654	0.54
170.0012	0.48	367.0169	0.31	363.0531	0.15	475.0711	1.68
174.0018	0.46	368.0147	0.31	368.0395	1.09	476.0625	11.39
180.9939	0.40	369.0223	0.68	377.0613	0.36	477.0872	100.00
183.0027	0.37	386.0146	0.42	379.0560	0.35	478.0948	12.64
184.0167	0.50	367.0108	0.31	381.1554	0.51	479.0916	1.01
185.0031	0.31	364.0315	0.56	382.0519	2.23	481.0321	0.16
188.0037	0.58	369.0244	0.51	383.0658	0.48	926.2225	4.64
191.9968	1.15	371.0149	0.56	387.0538	1.33	927.2615	2.09
193.0014	1.01	378.0163	0.41	388.0551	0.42		
195.0014	0.66	380.0089	5.93	389.0813	0.74		

37) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine

RMM 505 (58)



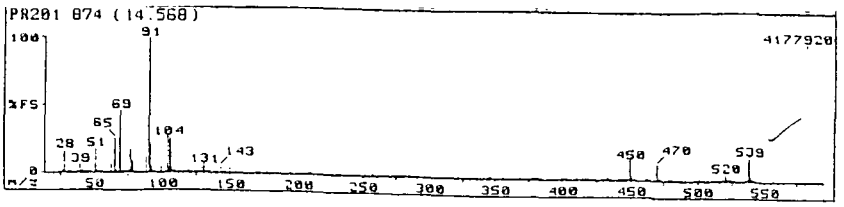
Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.11	79	0.20	133	0.14	188	0.07
22	0.04	80	0.24	135	0.04	189	0.07
24	0.15	81	0.94	136	0.08	190	0.08
26	5.76	82	0.55	137	0.14	191	0.07
27	29.38	83	0.61	138	0.52	193	0.29
28	22.21	84	0.41	139	0.10	194	0.03
29	69.48	85	0.51	140	0.11	195	0.08
30	2.00	86	0.23	141	0.11	196	0.23
31	8.60	87	0.15	142	0.23	197	0.05
32	0.29	88	0.42	143	0.96	198	0.08
33	0.53	89	0.21	144	0.10	200	0.47
35	0.08	90	0.12	145	0.34	201	0.11
36	0.14	91	0.41	146	0.15	202	0.07
37	0.20	92	0.48	147	0.07	203	0.14
38	0.77	93	2.03	148	0.10	204	0.06
39	1.08	94	0.27	149	0.23	205	0.19
40	1.38	95	0.34	150	1.15	207	0.46
41	3.55	96	0.13	151	0.22	208	0.24
42	6.17	97	0.23	152	0.13	209	0.10
43	1.28	98	0.13	153	0.17	210	0.11
44	2.24	99	0.67	154	0.10	211	0.06
45	0.76	100	1.00	155	0.35	212	0.15
46	0.51	101	0.32	156	0.08	213	0.09
47	0.44	102	0.13	157	0.15	214	0.07
48	0.06	103	0.06	158	0.17	215	0.12
50	4.75	104	0.10	159	0.11	217	0.15
51	1.94	105	0.33	160	0.14	218	0.11
52	0.69	106	0.12	161	0.06	219	0.07
53	1.90	107	0.44	162	0.24	220	0.11
54	2.38	108	0.42	163	0.08	221	0.12
55	2.38	109	0.09	164	0.08	222	0.13
56	5.01	110	0.17	165	0.22	223	0.10
57	1.51	111	0.17	166	0.05	224	0.12
58	0.82	112	0.40	167	0.15	227	0.30
59	0.30	113	0.24	168	0.12	228	0.08
60	0.14	114	0.22	169	0.42	230	0.04
61	0.10	115	0.29	170	0.30	231	0.15
62	0.53	116	0.08	171	0.09	232	0.10
63	0.36	117	0.33	172	0.05	233	0.08
64	0.54	118	0.11	173	0.14	235	0.12
65	0.52	119	0.49	174	0.15	238	0.28
66	0.50	120	0.11	175	0.09	239	0.16
67	0.84	121	0.05	176	0.37	240	0.08
68	17.53	122	0.06	177	0.31	241	0.10
69	100.00	123	0.17	178	0.10	242	0.11
70	1.81	124	0.79	179	0.07	243	0.10
71	0.73	125	0.14	180	0.05	245	0.10
72	0.37	126	0.14	181	0.17	246	0.10
73	0.39	127	0.16	182	0.09	247	0.16
74	1.17	128	0.11	183	0.09	248	0.10
75	0.87	129	0.08	184	0.10	249	0.09
76	0.72	130	0.20	185	0.08	250	0.15
77	0.60	131	0.71	186	0.07	252	0.10
78	0.17	132	0.20	187	0.05	253	0.08

Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
254	0.19	288	0.08	343	0.09	434	0.09
255	0.12	292	0.21	345	0.17	436	0.19
257	0.31	295	0.13	346	0.58	442	0.09
258	0.16	298	0.29	347	0.10	452	0.10
260	0.09	299	0.12	348	0.08	462	1.91
262	0.07	300	0.08	357	0.04	463	0.13
265	0.31	302	0.08	373	0.14	471	0.09
266	0.13	304	0.15	374	0.38	475	0.26
267	0.16	305	0.19	386	0.25	476	0.31
268	0.12	308	0.06	387	0.06	477	0.07
269	0.10	316	0.05	388	0.22	485	0.59
270	0.09	317	0.21	393	0.36	486	1.09
273	0.21	318	0.24	396	0.08	487	0.14
274	0.12	319	0.08	401	0.08	490	4.35
276	0.11	321	0.04	402	0.14	491	0.46
277	0.57	324	0.14	406	0.09	501	0.08
278	0.15	327	0.10	407	0.16	505	1.98
279	0.08	329	0.06	415	0.06	505	0.49
280	0.37	336	0.06	416	0.06	506	0.87
285	0.18	337	0.10	420	0.06		
286	0.10	338	0.09	421	0.14		

38) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine

RMM 539

(59)

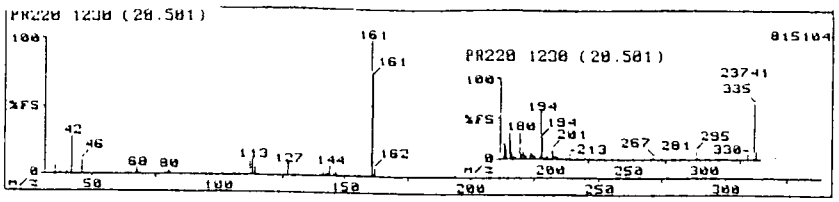


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.14	83	1.38	144	0.34	202	0.33
24	0.02	84	1.14	145	1.50	203	0.55
25	0.04	85	0.34	146	1.12	204	0.56
26	0.38	86	0.23	147	0.39	205	1.06
27	1.52	87	0.42	148	0.27	206	0.15
28	5.78	89	12.06	150	4.56	207	2.03
29	0.66	91	100.00	151	0.93	208	1.07
30	0.22	92	21.18	152	1.16	209	1.66
31	1.19	93	3.92	153	0.81	210	2.35
32	0.20	94	0.24	154	0.08	211	0.30
33	0.06	95	0.40	155	1.84	212	0.53
36	0.03	96	0.43	156	0.58	213	0.25
37	0.20	97	0.26	157	0.82	214	0.34
38	0.92	98	0.10	158	1.45	215	0.55
39	7.16	100	5.20	159	0.38	216	0.25
40	0.87	101	0.63	160	2.62	217	0.27
41	1.50	102	1.05	161	0.32	218	0.04
42	0.23	103	7.25	162	0.81	219	0.31
43	0.13	104	27.45	163	0.20	220	0.40
44	0.14	105	3.55	164	0.46	221	0.38
45	0.11	106	25.10	165	1.84	222	0.57
46	0.39	107	3.43	166	1.15	223	0.28
47	0.03	108	1.39	167	0.61	224	0.50
50	3.24	109	2.48	169	2.18	225	0.78
51	6.86	110	0.96	170	1.53	226	0.80
52	1.74	112	0.66	171	0.69	227	2.21
53	1.05	113	0.26	172	0.44	228	0.55
54	0.40	114	0.61	173	0.60	229	0.34
55	0.58	115	1.56	174	0.77	230	0.38
56	0.08	116	2.23	175	0.75	231	0.92
57	0.35	117	1.37	176	3.72	232	0.49
58	0.29	118	0.15	177	1.05	233	0.38
59	0.09	119	2.35	178	0.34	234	0.22
60	0.03	120	0.61	179	0.08	235	1.08
61	0.19	121	0.36	180	1.91	236	0.20
62	1.39	122	0.21	182	1.24	237	0.06
63	6.37	124	1.81	183	1.34	238	0.72
64	1.42	125	0.59	184	0.29	239	0.61
65	25.10	126	0.70	185	0.38	240	0.31
66	1.48	127	1.07	186	0.51	241	0.22
67	0.16	128	0.41	187	0.25	242	0.42
69	46.27	129	3.53	188	0.75	243	0.54
70	1.35	131	6.57	189	0.55	244	0.04
71	0.35	132	0.86	190	0.83	245	1.43
72	0.06	133	1.16	191	0.51	246	0.27
73	0.19	134	0.58	192	0.11	247	0.44
74	1.48	135	0.22	193	1.32	248	0.12
75	1.64	136	0.22	194	0.15	250	0.77
76	3.77	137	0.16	195	1.99	251	0.14
77	17.55	138	1.81	196	1.04	252	0.42
78	8.73	139	0.39	197	0.34	253	0.37
79	7.84	140	0.56	198	0.19	254	0.52
80	0.77	141	0.51	200	2.16	255	0.36
81	0.37	143	5.32	201	0.87	257	2.13

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
256	1.57	314	0.10	369	0.13	431	0.34
257	0.54	315	0.22	370	0.48	432	0.09
260	0.74	316	0.22	371	0.12	433	2.92
261	0.34	317	0.09	372	0.55	434	0.53
262	0.35	318	0.02	373	0.50	435	0.32
263	0.12	319	0.08	374	0.30	436	0.04
264	0.18	320	0.03	375	0.65	440	0.02
265	1.34	321	0.07	376	0.16	441	0.05
266	0.21	322	0.17	377	0.05	442	0.21
267	0.30	323	0.17	378	0.13	443	0.08
268	0.65	324	0.44	379	0.13	444	0.02
270	1.67	325	0.07	380	1.10	445	0.03
271	0.21	326	0.12	381	2.30	446	0.01
272	0.42	327	0.40	382	0.59	447	0.03
273	0.40	328	0.31	383	0.09	448	0.26
274	0.39	329	0.18	384	0.03	449	0.18
275	0.08	330	0.36	385	0.03	450	15.78
276	0.16	331	0.66	386	0.01	451	3.24
277	1.72	332	0.18	388	0.02	452	0.33
278	0.78	333	0.14	390	0.06	453	0.06
279	0.93	334	0.17	391	0.11	454	0.02
280	0.65	335	0.11	392	0.09	455	0.01
281	0.45	336	0.05	393	0.83	460	0.91
282	0.16	338	0.03	394	0.11	461	0.14
283	0.22	339	0.06	395	0.25	462	2.69
284	0.17	340	0.29	396	0.45	463	0.45
285	0.57	341	0.34	397	0.07	464	0.04
286	0.19	342	0.16	398	0.09	467	0.06
287	0.04	343	0.40	399	0.10	468	0.39
288	0.22	344	0.03	400	0.74	469	1.21
289	0.13	345	1.95	401	0.23	470	11.18
290	0.26	346	2.25	402	0.10	471	2.21
291	0.35	347	0.47	403	0.07	472	0.22
292	0.93	348	0.08	404	0.05	473	0.02
293	0.11	349	0.05	405	0.02	478	0.02
295	1.05	350	0.26	408	0.01	479	0.01
296	0.20	351	0.07	409	0.03	480	0.21
297	1.37	352	0.07	410	0.22	481	0.06
298	0.17	353	0.27	411	0.07	482	0.02
299	0.11	354	0.11	412	0.10	498	0.03
300	0.55	355	0.15	413	0.02	499	0.04
301	0.24	356	0.03	414	0.11	500	0.70
302	0.06	357	0.02	415	0.12	501	0.17
303	0.37	358	0.08	416	0.06	502	0.03
304	0.45	359	0.12	417	0.05	511	0.06
305	0.39	360	0.54	418	0.05	512	0.03
306	0.05	361	0.31	419	0.31	518	0.11
307	0.26	362	0.98	420	0.07	519	3.55
308	0.14	363	0.19	422	0.14	520	5.76
309	0.20	364	0.23	423	0.20	521	1.17
310	0.58	365	0.20	424	0.05	522	0.14
311	0.52	366	0.44	428	0.07	523	0.02
312	0.56	367	0.08	429	0.07	524	0.01
313	0.12	368	0.05	430	0.42	536	0.08

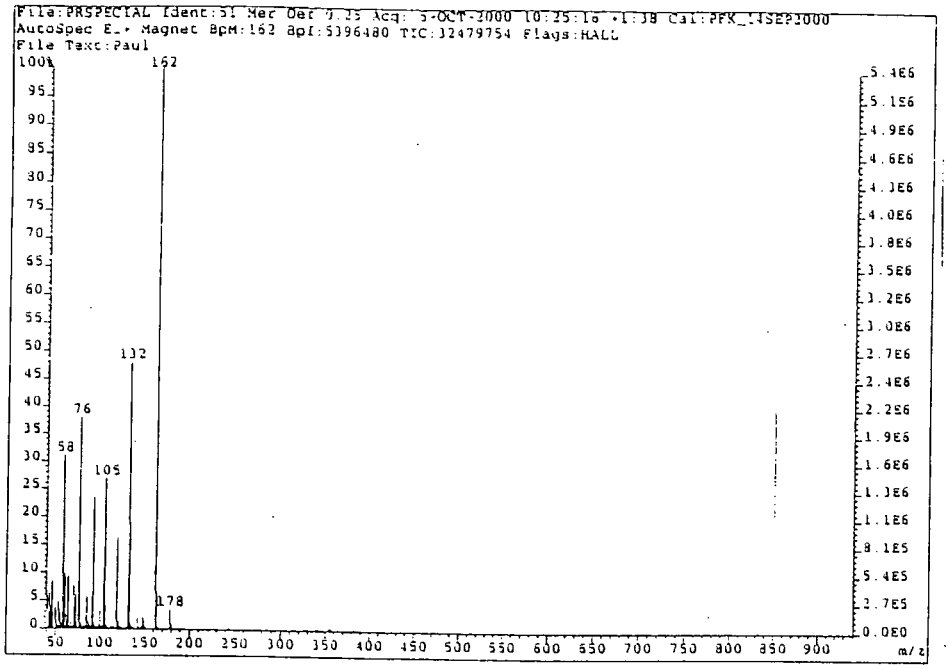
39) 2,5,6-trifluoro-4-methoxypyrimidine

RMM 164 (60)



Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
35	5.56	80	4.30	115	1.19	155	1.24
37	1.76	81	1.52	127	8.67	156	1.69
40	1.96	85	1.27	131	1.76	158	1.41
42	28.52	94	1.44	141	1.05	159	1.04
46	9.67	96	1.28	141	1.05	161	100.00
64	1.10	98	1.23	142	1.33	161	72.36
64	1.32	102	1.42	143	2.98	162	5.59
68	2.83	106	1.74	144	7.85	194	1.74
68	5.18	112	10.30	146	1.17	335	1.99
79	2.54	113	12.06	146	1.52		
80	1.48	114	5.46	151	1.01		

40) 2,5-difluoro-6-hydroxy-4-methoxypyrimidine RMM 162 (61)

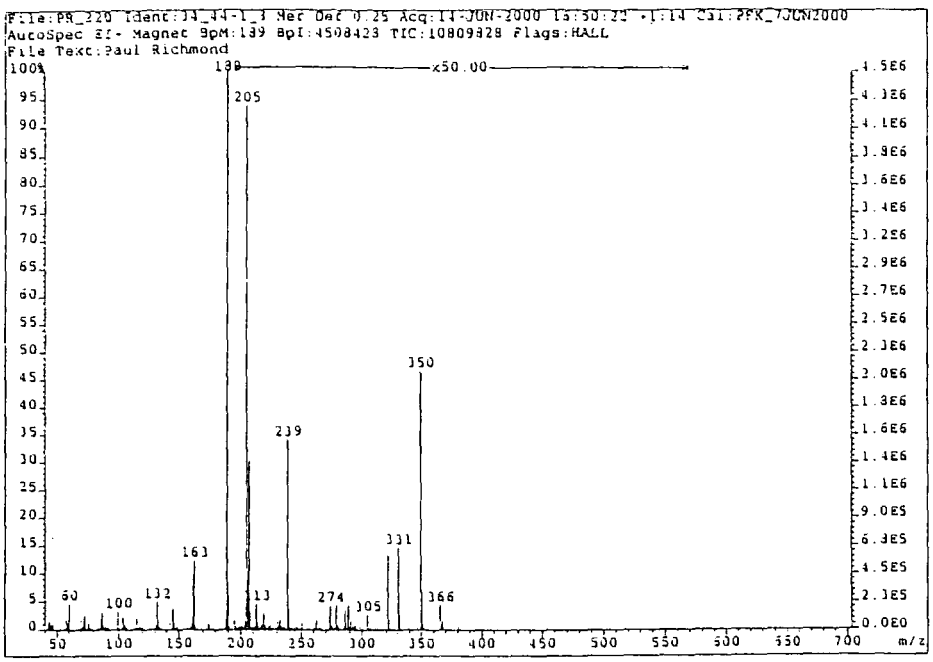


ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT
41.1400	5.33	75.1571	0.34	107.2561	0.61	149.3033	1.40
42.1404	3.39	76.1577	10.53	108.3267	0.84	150.2900	0.77
43.1407	6.40	77.1081	6.37	109.3102	0.42	151.3911	0.26
44.1349	3.84	78.2106	1.15	110.2938	0.44	161.3194	10.86
45.1527	3.42	79.2321	1.06	111.3507	0.14	162.3291	100.00
46.1510	8.69	80.2395	0.15	112.2845	1.17	163.3253	4.74
47.1352	3.31	81.2731	1.07	113.3307	0.58	164.3330	0.64
50.1464	1.05	82.3806	0.37	114.3752	0.11	167.3448	0.38
51.1578	1.66	83.3672	1.01	115.3798	1.36	177.3202	0.60
52.1662	0.76	84.3351	2.13	116.3638	0.40	178.3146	3.59
53.1702	4.36	85.3201	5.49	117.3610	2.85	179.3245	0.67
54.1591	3.41	86.3334	1.47	118.3748	16.52	180.3156	1.23
55.2109	2.62	87.2470	1.28	120.3798	1.43	243.1739	0.81
56.2087	1.27	88.2242	0.81	121.2971	1.54	264.6560	0.73
57.1784	11.21	89.2378	0.68	122.3756	0.61	284.3488	0.10
58.1920	34.16	90.2312	5.53	123.3123	0.57	339.4326	0.30
59.1851	4.74	91.2442	0.25	128.2737	0.46	340.4370	0.18
60.1929	9.88	92.3170	33.61	129.3616	0.66	341.4314	0.63
61.1998	0.61	93.3417	1.32	130.3718	1.47	351.4416	1.71
62.1694	2.71	94.3231	0.77	131.3783	10.21	354.4419	1.37
63.1570	1.35	95.3065	0.77	132.3879	68.05	355.4368	3.23
64.1894	9.43	96.3138	0.41	133.3968	10.97	356.4659	0.45
65.1989	0.71	97.3278	0.49	134.3965	1.28	367.4083	0.64
66.1419	0.62	98.3191	0.54	135.3806	0.91	381.4607	0.49
67.2251	1.28	99.3471	0.32	136.3570	9.33	382.3751	0.42
68.2103	0.82	100.2448	1.22	137.3467	0.63	446.5370	0.23
69.2480	3.85	101.2596	0.58	142.2037	3.14	449.3810	1.53
70.1870	3.48	102.2383	0.24	143.2156	0.50	649.3745	1.24
71.2070	5.18	103.2493	1.51	145.3231	0.46	650.4449	0.31
73.2317	5.65	104.2573	10.91	146.2870	1.05	708.3333	1.24
74.1951	4.36	105.3417	36.35	147.2791	0.67	709.3886	0.35
74.2085	1.20	106.2506	4.24	148.2788	2.14		

41) 6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine

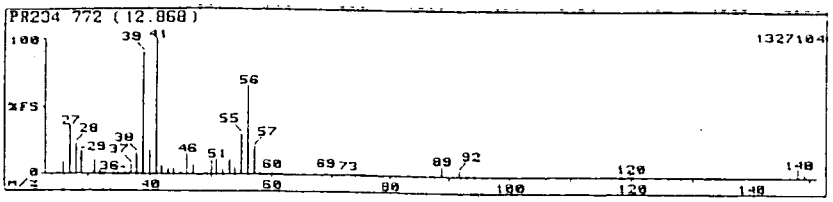
RMM 350

(62)



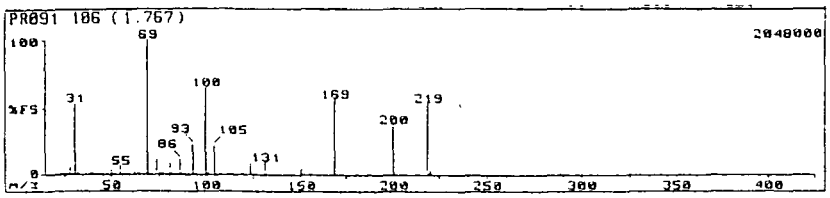
ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT	ABS MASS	REL (%) HEIGHT
60.9663	0.12	79.9717	0.12	119.9594	0.69	168.9625	0.67
61.9844	1.08	80.9996	0.18	120.9520	0.22	169.9680	0.09
62.9942	1.64	81.9955	0.11	121.9597	0.10	171.9611	0.09
63.9906	1.56	83.0056	0.97	126.9824	0.73	172.9740	0.17
64.9740	0.86	83.9932	0.44	127.9854	0.34	173.9982	1.18
65.9631	1.08	84.9940	1.06	128.9894	0.26	174.9700	1.01
66.9648	0.93	85.9967	1.45	129.9963	0.85	175.9694	0.19
67.9527	0.23	86.9691	1.18	130.9823	1.17	176.9619	0.17
68.9824	0.23	87.9632	0.95	131.9810	5.12	177.9611	0.24
69.9750	0.27	88.9676	0.14	132.9813	1.77	178.9585	3.26
70.9772	0.30	89.9687	0.43	133.9565	0.53	179.9571	0.14
71.9818	0.56	90.9735	0.50	134.9674	0.31	180.9316	0.11
72.9819	0.38	91.9521	0.71	139.9641	0.10	181.9962	0.08
73.9819	0.41	93.9847	0.11	140.9694	0.24	185.9671	0.10
74.9916	1.30	94.9887	0.22	141.9568	0.19	186.9789	1.01
75.9809	1.52	95.9854	0.25	142.9613	1.41	187.9874	1.12
76.9827	1.24	97.0138	0.59	143.9574	0.22	188.9494	100.00
77.9818	4.89	97.9895	0.17	144.9888	4.08	189.9512	8.67
78.9871	0.85	98.9563	0.59	145.9664	1.12	190.9550	3.75
79.9835	0.14	99.9688	1.48	146.9522	0.27	191.9671	0.08
82.9770	0.08	100.9671	0.39	147.9781	0.48	202.9701	0.09
84.9816	0.15	101.9569	0.37	148.9649	0.73	203.9756	0.12
85.9777	0.06	102.9689	0.76	149.9754	0.17	204.9739	1.88
86.9693	0.28	103.9687	7.46	153.9582	0.13	205.9714	0.21
87.9653	0.23	104.9658	1.18	155.9761	0.35	206.9728	0.01
88.9885	0.56	105.9681	0.80	156.9645	0.19	212.9500	0.09
89.9765	1.76	106.9669	0.42	157.9699	0.74	218.9400	0.69
90.9877	0.25	110.9691	0.38	159.9731	0.80	231.9748	0.05
91.9821	3.49	111.9824	0.36	159.9836	1.25	274.9306	0.09
92.9596	2.58	112.9736	0.57	160.9594	2.12	288.9287	0.09
93.9648	0.36	113.9518	3.58	161.9631	4.71	321.9724	0.27
94.9809	0.21	114.9532	1.31	162.9509	12.18	330.9782	0.10
95.9585	1.19	115.9528	1.58	163.9512	0.43	349.9678	0.74
96.9713	0.49	116.9676	0.57	164.9664	0.13	350.9705	0.11
97.9675	0.53	117.9664	1.39	166.9748	0.22	365.9527	0.09
98.9676	0.13	118.9694	0.56	167.9960	0.09		

42) 4,6-bis(tert-butoxy)-2,5-difluoropyrimidine RMM 260 (63)

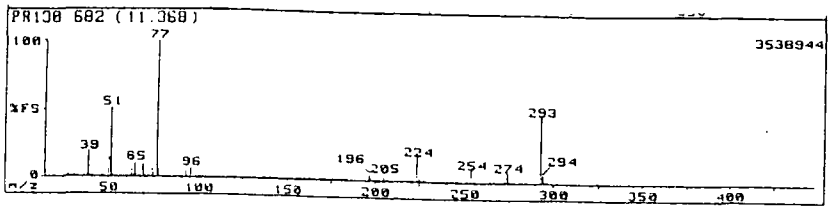


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
25	1.09	38	15.56	49	2.16	60	3.72
26	8.80	39	90.12	50	10.03	69	4.42
27	35.49	40	17.13	51	11.88	73	3.35
28	22.22	41	100.00	52	3.80	74	1.23
29	16.20	42	5.40	53	10.42	87	1.43
31	9.34	43	4.21	54	5.02	89	7.41
32	1.81	44	4.94	55	30.25	92	4.30
35	1.41	45	1.93	56	66.05	120	3.11
36	2.41	46	15.59	57	20.37	148	7.02
37	7.18	47	7.10	58	1.54	149	2.50

43) 2,3,5,6-tetrafluoro-4-trifluoromethylpyridine RMM 219 (64)



44) 3,5,6-trifluoro-2-phenoxy-4-trifluoromethylpyridine RMM 293 (65)

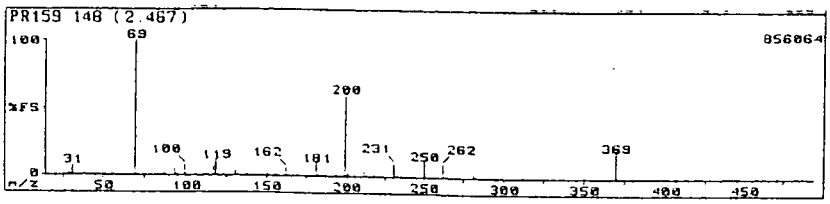


Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.04	85	0.13	152	0.22	220	0.13
25	0.02	86	1.25	151	0.05	221	0.01
26	0.43	87	0.21	155	0.19	224	13.75
27	2.11	88	0.31	156	0.10	225	2.58
28	2.40	89	0.19	157	0.12	226	0.71
29	0.13	90	0.15	158	0.41	227	0.10
31	2.34	91	0.08	159	0.09	228	0.07
32	0.67	93	5.15	160	0.02	229	0.02
33	0.05	94	0.44	161	0.31	230	0.02
36	0.04	96	7.52	162	0.22	232	0.07
37	1.34	97	0.53	163	0.05	234	0.04
38	4.75	98	0.10	164	0.07	235	0.01
39	19.56	99	0.84	165	0.06	236	0.03
40	0.75	100	2.00	166	0.05	238	0.20
41	0.25	101	0.16	167	0.04	239	0.05
42	0.19	102	0.09	169	2.40	241	0.02
44	0.65	103	0.14	170	0.67	242	0.03
44	0.48	105	1.72	171	0.06	243	0.08
45	0.14	106	0.19	172	0.01	244	0.38
46	0.17	107	0.39	174	0.28	245	0.85
47	0.18	108	0.13	175	2.69	246	1.37
50	14.47	109	0.17	177	0.11	247	0.51
51	51.39	110	0.08	178	0.15	248	0.11
52	2.08	112	0.82	179	0.20	250	0.05
53	0.78	113	0.09	181	1.45	251	0.02
54	0.18	114	0.17	182	0.17	252	0.03
55	0.61	115	0.02	193	1.34	254	9.38
56	0.13	117	1.42	184	0.27	255	0.95
57	0.56	118	0.08	186	0.76	256	0.09
58	0.06	119	0.45	187	0.11	260	0.03
59	0.04	120	0.11	188	0.46	262	0.01
60	0.08	121	0.14	189	0.08	264	1.74
61	0.67	123	0.25	192	0.04	265	2.23
62	2.72	124	2.03	194	0.65	266	0.22
63	5.53	125	0.12	196	5.21	267	0.09
64	1.81	127	0.94	197	1.24	272	2.11
65	11.57	129	0.01	198	0.28	273	4.43
66	0.71	131	1.32	200	1.18	274	8.22
67	0.12	132	0.19	201	0.14	275	0.82
69	10.07	134	0.31	203	0.19	276	0.07
70	0.31	136	2.37	204	1.16	278	0.02
71	1.01	137	0.25	205	6.08	281	0.02
72	0.04	138	0.99	206	1.01	293	50.00
73	0.71	139	0.16	207	0.18	294	5.73
74	5.76	140	0.05	208	0.09	295	0.41
75	3.33	141	0.02	209	0.04	296	0.03
77	100.00	143	0.41	212	0.07	324	0.01
78	5.44	144	0.06	214	0.12	325	0.01
79	0.31	145	0.15	215	0.19	343	0.02
80	0.09	146	0.56	216	0.01	370	0.01
81	0.67	149	0.16	217	0.02	376	0.01
82	0.24	150	1.13	218	0.08	443	0.00
83	0.23	151	0.68	219	0.19		

45) 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine

RMM 369

(66)

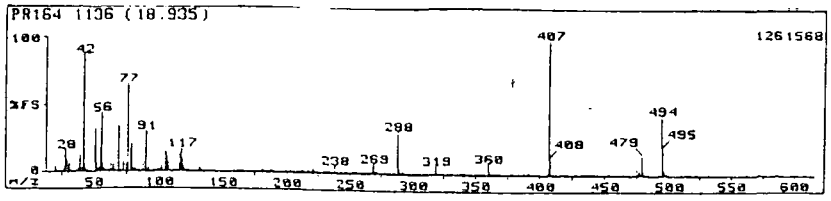


Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.26	69	100.00	131	4.07	201	2.72
24	0.03	70	0.96	132	0.18	202	0.07
25	0.02	74	1.32	136	1.23	205	0.46
26	0.22	75	0.13	137	0.06	206	0.03
27	0.14	76	0.48	138	0.13	212	4.04
28	1.26	78	0.02	141	0.03	213	0.24
29	0.11	79	0.62	143	0.29	217	0.15
31	7.78	81	1.38	144	0.06	219	0.04
32	0.27	82	0.21	148	0.71	224	0.43
35	0.07	85	0.15	150	2.81	231	10.17
36	0.12	86	1.76	151	0.13	233	0.02
37	0.09	87	0.16	155	1.38	236	0.23
38	0.12	88	0.14	156	0.06	243	0.05
39	0.03	93	4.99	162	5.62	250	11.96
40	0.06	94	0.10	163	0.31	251	0.73
41	0.03	95	0.03	167	0.60	255	0.05
42	0.07	98	0.76	169	0.83	262	9.57
43	0.19	100	8.01	170	0.05	263	0.61
44	0.10	101	0.30	174	0.10	264	0.02
45	0.07	105	2.15	178	0.06	281	1.08
47	0.54	106	0.11	179	0.06	282	0.22
48	0.03	107	0.05	181	10.05	300	0.84
50	2.69	110	0.06	182	0.81	312	0.09
51	0.29	112	1.17	183	0.03	331	0.29
55	0.55	113	0.16	186	1.11	350	1.37
56	0.08	114	0.16	187	0.06	351	0.18
57	0.06	117	7.42	193	1.56	369	19.14
62	0.36	119	12.08	194	0.10	400	0.14
63	0.08	120	0.19	197	0.11	438	0.73
66	0.27	124	2.03	198	0.03	488	0.02
67	0.11	129	0.14	200	59.81		

46) (1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol

RMM 514

(67)



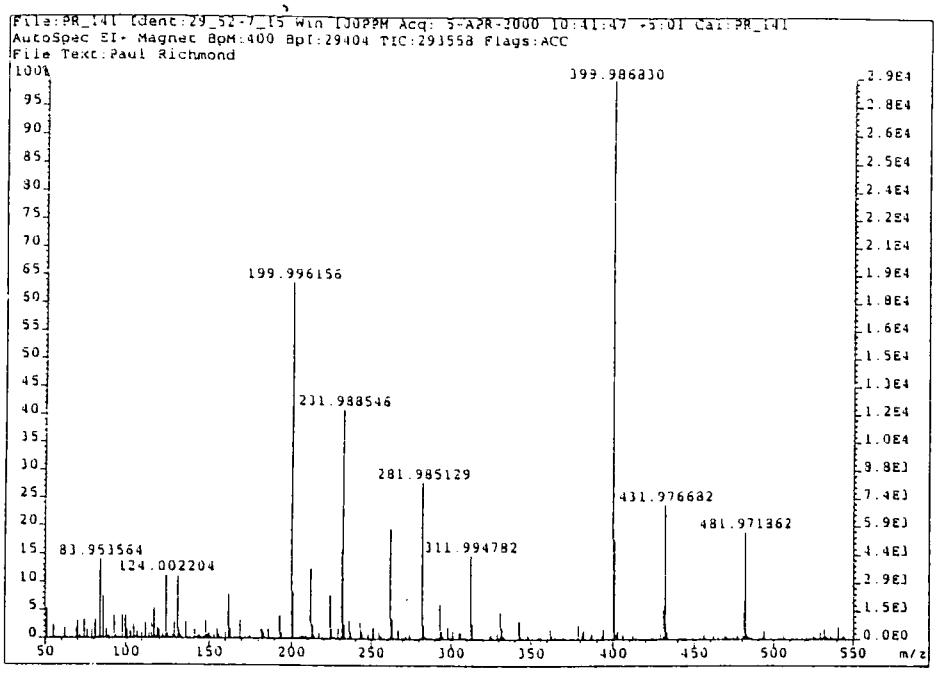
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	3.98	79	20.62	134	0.64	188	2.29
21	0.13	80	1.58	135	0.52	189	1.12
24	0.45	81	1.46	136	0.50	190	1.10
25	0.79	82	1.02	137	0.64	191	0.65
26	5.13	83	1.05	138	0.41	192	0.43
27	12.58	84	0.28	139	0.36	193	1.29
28	16.48	85	0.55	140	0.48	194	0.92
29	8.36	86	0.63	141	0.63	195	1.02
30	4.36	87	0.99	142	0.66	196	0.78
31	5.76	88	0.47	143	1.15	197	0.62
32	0.50	89	7.79	144	1.29	198	0.67
33	0.53	91	30.52	145	0.92	199	1.46
35	1.01	92	2.72	146	1.02	200	1.48
36	1.87	93	3.33	147	0.58	201	1.19
37	2.60	94	0.78	148	0.50	202	1.28
38	4.53	95	0.53	149	0.47	203	1.70
39	12.66	96	1.07	150	0.79	204	0.90
40	3.06	97	0.17	151	0.71	205	1.30
41	4.20	98	0.60	152	0.50	206	0.96
42	87.01	99	0.81	153	0.36	207	0.73
43	4.95	100	4.32	154	0.87	208	0.76
44	1.38	101	0.95	155	1.54	209	0.60
45	0.56	102	2.27	156	0.47	210	1.83
46	0.61	103	6.74	157	0.49	211	0.56
47	1.05	104	9.25	158	0.53	212	2.64
48	0.52	105	15.99	159	0.47	213	2.21
49	0.53	106	10.88	160	0.61	214	0.48
50	18.67	107	6.41	161	0.92	215	0.57
51	32.14	108	0.70	162	1.91	216	0.26
52	6.74	109	0.66	163	1.07	217	2.58
53	2.82	110	0.13	164	0.82	218	0.80
54	3.45	111	0.37	165	0.48	219	0.51
55	1.27	112	0.81	166	0.48	220	2.70
56	18.59	113	0.98	167	1.01	221	4.08
57	43.83	114	5.68	168	1.19	222	1.36
58	6.25	115	13.31	169	1.29	223	0.37
59	2.09	116	11.44	170	1.20	224	1.42
60	0.30	117	17.66	171	0.93	225	0.44
61	0.90	118	9.25	172	0.77	226	0.78
62	0.53	119	4.30	173	0.65	227	0.96
63	2.07	120	0.63	174	1.07	228	0.87
64	6.09	121	0.31	175	0.94	229	0.99
65	1.40	122	0.29	176	0.90	230	0.52
66	4.61	123	0.75	177	0.84	231	1.68
67	0.89	124	1.19	178	0.90	232	1.64
68	0.46	125	0.53	179	0.48	233	0.63
69	33.77	126	0.53	180	0.99	234	0.78
70	0.88	127	0.72	181	3.06	235	0.66
71	0.30	128	0.86	182	1.77	236	1.24
72	0.29	129	1.38	183	0.72	237	0.55
74	6.49	130	2.48	184	0.67	238	5.76
75	4.67	131	1.51	185	0.81	238	4.57
77	65.26	132	1.72	186	1.08	239	0.72
78	16.23	133	1.16	187	1.79	240	1.11

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
241	1.09	294	0.27	348	0.33	403	0.65
241	1.23	295	1.17	349	0.56	404	0.06
243	1.64	296	0.24	350	0.74	405	1.36
244	1.02	297	0.59	351	0.40	406	4.42
244	1.14	298	1.24	352	0.18	407	100.00
246	2.15	298	1.21	353	0.51	408	12.50
247	1.60	299	0.70	354	0.15	409	0.61
247	2.19	300	0.51	355	0.50	410	0.24
248	1.08	302	0.33	356	1.03	411	0.08
250	1.06	303	1.11	357	0.37	412	0.01
251	1.10	304	0.42	358	0.16	413	0.03
251	0.87	305	0.42	360	8.85	414	0.02
253	1.50	306	0.17	361	1.95	416	1.18
253	1.64	307	0.15	362	0.28	417	1.35
255	1.66	308	0.17	363	0.07	418	0.53
255	1.23	309	0.34	364	0.38	419	0.18
256	0.49	310	1.87	365	2.19	420	0.04
257	0.72	311	0.70	366	0.16	421	0.07
256	0.87	312	0.38	367	0.43	422	0.04
259	1.32	313	0.75	368	0.43	423	0.05
260	1.22	314	0.34	369	0.98	424	0.05
261	1.30	315	0.21	370	0.17	425	0.37
262	1.68	316	0.29	371	0.10	426	0.11
263	1.10	317	1.42	372	0.04	427	0.04
264	0.53	318	0.98	373	0.34	428	0.02
265	0.33	319	6.49	374	1.09	429	0.04
267	1.20	320	1.00	375	1.46	431	0.08
267	1.62	321	0.29	376	0.34	432	0.07
269	7.22	322	0.19	377	0.88	433	0.06
269	7.31	323	0.26	378	0.49	434	0.13
270	2.07	324	0.39	379	0.82	435	0.15
271	1.60	325	0.34	380	0.74	436	0.21
272	1.81	326	0.38	381	0.29	437	0.34
273	1.56	327	0.80	382	0.07	438	0.27
274	0.96	328	0.16	383	0.02	439	0.15
275	0.51	329	0.68	384	0.02	440	0.09
276	0.34	330	0.08	385	0.10	441	0.83
277	1.60	331	0.74	386	0.19	442	0.17
278	1.46	332	0.94	387	1.18	443	0.05
279	1.06	333	0.13	388	2.27	444	0.04
281	0.55	334	0.22	389	1.07	445	0.10
281	0.51	335	0.12	390	0.07	446	0.04
282	0.47	336	0.14	391	3.29	447	0.06
283	0.57	337	0.26	392	0.91	448	0.03
284	0.45	338	1.06	393	0.96	449	0.04
285	0.13	339	0.55	394	0.12	450	0.20
286	2.07	340	0.32	395	0.02	451	0.14
287	0.93	341	3.21	396	0.03	452	0.10
288	12.47	342	0.73	397	0.08	453	0.05
289	3.65	343	0.51	398	0.10	454	0.27
290	1.32	344	0.20	399	0.15	455	0.23
291	0.87	345	1.38	400	0.07	456	1.15
292	0.35	346	0.35	401	0.05	457	0.64
293	1.62	347	0.54	402	0.27	458	0.14
459	0.27	477	3.45	497	2.07	545	0.05
460	0.05	478	1.32	498	0.37	563	0.09
461	0.34	479	14.69	499	0.06	571	0.11
462	0.27	480	2.70	509	0.04	572	0.04
463	1.40	481	0.42	510	0.02	573	0.03
464	0.37	482	0.07	511	0.02	585	0.13
465	0.13	483	0.08	512	0.03	586	0.04
467	0.03	490	0.02	513	0.11	587	0.03
469	0.06	491	0.07	514	0.03	599	0.05
472	0.02	492	0.20	515	0.08	600	0.02
473	0.12	493	1.07	516	0.03	609	0.02
474	0.13	494	44.81	521	0.02		
475	4.87	495	20.78	523	0.03		
475	1.79	496	3.73	533			

47) 3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]benzene-1,2-dicarbonitrile

RMM 400

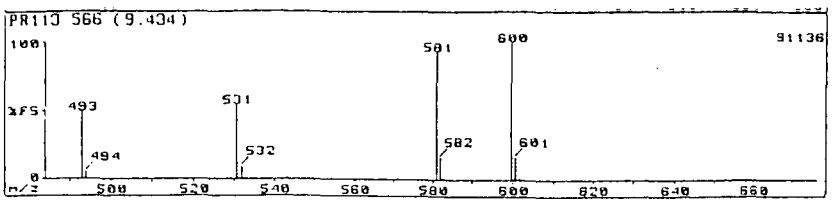
(68)



48) 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile

RMM 600

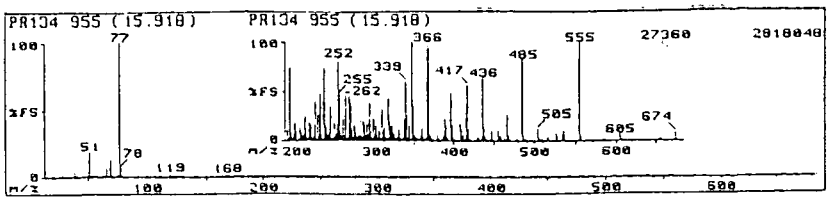
(69)



Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc	Mass	Rel Inc
20	0.07	120	0.27	215	0.02	310	0.12
26	0.04	122	0.12	217	0.95	312	11.06
27	0.03	124	1.82	218	0.05	313	1.18
28	0.79	125	0.13	219	0.02	314	0.10
29	0.02	127	0.01	222	0.08	317	0.15
31	2.04	129	0.44	224	5.03	318	0.03
32	0.23	131	1.15	225	0.30	324	0.44
36	0.02	132	0.05	226	0.04	325	0.10
38	0.01	134	0.05	229	0.48	326	0.01
39	0.01	136	0.47	231	0.80	329	0.06
40	0.02	137	0.05	232	0.04	331	0.18
41	0.01	138	0.06	234	0.02	332	0.02
43	0.02	141	0.50	236	0.71	336	0.23
44	0.09	142	0.04	237	0.05	337	0.04
45	0.02	143	0.16	238	0.01	343	5.41
47	0.01	144	0.01	241	0.28	344	0.75
50	1.14	146	0.04	243	2.58	345	0.06
51	0.09	148	1.28	244	0.14	348	0.07
52	0.01	149	0.12	245	0.04	349	0.01
55	0.05	150	0.10	248	1.36	355	0.25
57	0.01	151	0.09	249	0.14	356	0.04
60	0.01	153	1.19	250	0.05	360	0.02
62	0.06	156	0.11	253	0.03	362	1.08
63	0.01	160	0.10	255	5.75	363	0.19
66	0.01	162	0.76	256	0.64	364	0.03
69	100.00	163	0.06	257	0.05	367	0.02
74	0.15	165	0.07	260	0.18	371	0.04
75	0.03	167	0.40	262	11.93	374	0.21
76	0.15	168	0.04	263	1.11	375	0.05
77	0.02	169	0.06	264	0.08	381	0.14
79	0.16	172	0.22	265	0.02	382	0.02
81	0.32	174	0.26	267	0.12	386	0.07
82	0.03	175	0.05	268	0.04	393	1.51
85	0.04	179	0.59	272	0.09	394	0.20
86	0.28	180	0.06	274	1.13	395	0.02
87	0.03	181	0.06	275	0.21	398	0.01
88	0.01	184	0.01	276	0.01	405	0.08
91	0.02	186	0.72	279	0.17	406	0.02
93	2.04	187	0.07	280	0.03	412	0.11
94	0.08	191	0.15	281	0.50	413	0.17
96	0.01	193	2.38	282	0.06	414	0.02
98	0.29	194	0.25	286	1.00	421	0.01
100	5.13	195	0.02	287	0.12	424	0.05
101	0.15	196	0.01	291	0.06	431	46.21
103	0.10	198	0.29	293	12.06	432	6.11
105	0.48	199	0.02	294	1.41	433	0.45
106	0.04	200	0.26	295	0.11	443	0.14
107	0.06	201	0.01	296	0.01	444	0.01
110	0.20	203	0.15	298	0.28	455	0.02
112	0.44	205	0.45	299	0.03	462	0.19
113	0.03	206	0.07	303	0.02	463	0.05
114	0.01	210	0.51	305	1.13	481	25.25
117	1.26	212	1.93	306	0.15	482	1.36
119	12.69	213	0.17	307	0.01	483	0.20
493	1.17	531	1.48	581	2.61	601	0.46
494	0.14	532	0.23	582	0.46	602	0.02
512	0.02	541	0.02	583	0.02	669	0.01
513	0.01	562	0.01	600	2.80		

49) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile

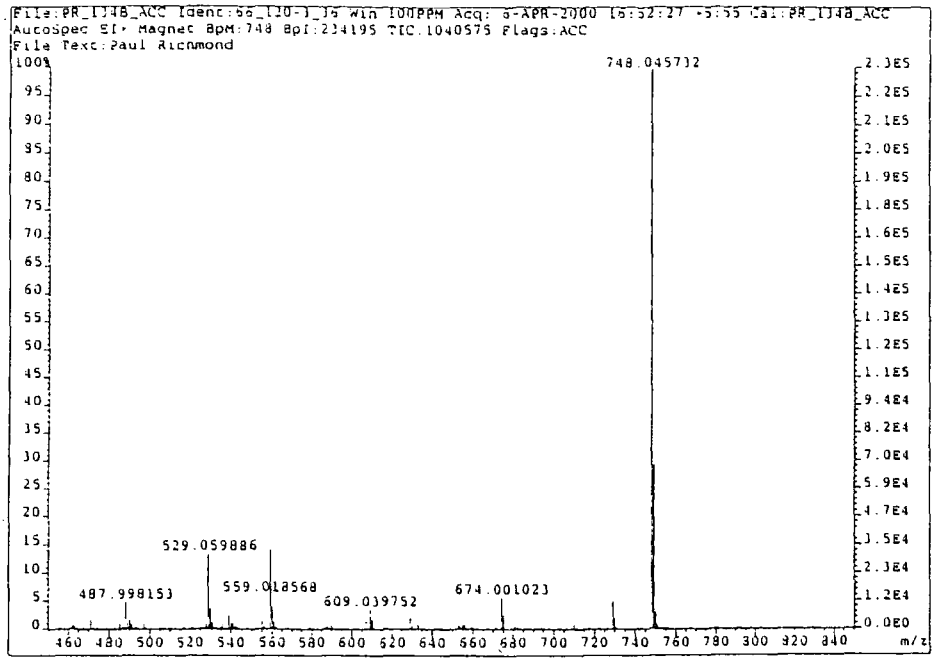
RMM 674 (70)



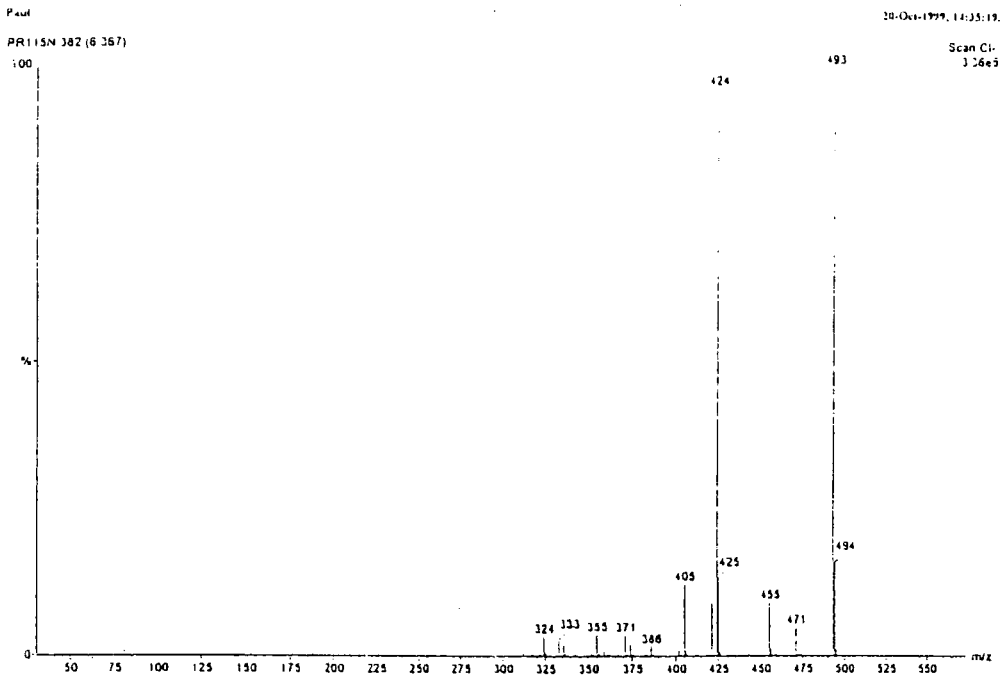
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
20	0.05	88	0.05	150	0.04	214	0.03
25	0.01	89	0.03	151	0.05	215	0.02
26	0.09	90	0.04	152	0.02	216	0.02
27	0.66	91	0.04	153	0.18	217	0.18
28	0.87	92	0.36	154	0.06	218	0.17
29	0.02	93	0.91	155	0.27	219	0.08
31	0.33	94	0.22	156	0.02	220	0.14
32	0.27	95	0.22	158	1.04	221	0.03
36	0.01	96	0.58	160	0.05	222	0.03
37	0.17	97	0.05	161	0.03	223	0.05
38	0.84	98	0.03	162	0.15	224	0.39
39	3.96	100	0.67	163	0.03	225	0.08
40	0.16	101	0.03	164	0.02	226	0.02
41	0.04	102	0.09	165	0.02	228	0.26
42	0.02	103	0.64	167	0.15	229	0.07
43	0.01	104	0.07	168	2.54	230	0.04
44	0.06	105	0.08	170	0.06	231	0.47
45	0.01	106	0.02	171	0.04	232	0.07
46	0.01	107	0.05	172	0.03	233	0.04
47	0.04	108	0.03	174	0.27	234	0.02
49	0.13	110	0.02	175	0.06	235	0.03
50	4.58	111	0.02	176	0.04	236	0.72
51	19.48	112	0.08	177	0.04	237	0.16
52	0.92	114	0.02	179	0.11	238	0.12
53	0.19	115	0.02	180	0.02	239	0.10
54	0.06	117	0.16	181	0.07	240	0.07
55	0.01	119	4.36	182	0.06	241	0.05
56	0.08	120	0.09	183	0.22	242	0.08
57	0.02	121	0.01	185	0.03	243	0.34
58	0.12	122	0.01	186	0.21	244	0.13
61	0.52	123	0.05	187	0.04	245	0.03
62	1.68	124	0.16	188	0.01	246	0.01
63	1.04	125	0.03	189	0.11	247	0.04
64	6.36	126	0.05	191	0.03	248	0.18
65	0.46	127	0.33	193	0.73	249	0.07
66	0.04	128	0.02	194	0.07	250	0.08
67	12.21	129	0.03	195	0.02	251	0.13
69	0.25	131	0.18	196	0.02	252	0.82
70	0.04	132	0.02	197	0.01	254	0.04
71	0.18	133	0.03	198	0.07	255	0.45
73	1.77	134	0.01	199	0.18	256	0.09
74	1.92	136	0.07	200	0.02	257	0.03
75	2.33	136	0.06	201	0.02	258	0.05
76	100.00	138	0.04	203	0.02	259	0.22
77	7.27	139	0.01	204	0.03	260	0.11
78	0.29	140	0.01	205	0.13	261	0.06
79	0.10	141	0.06	206	0.06	262	0.44
81	0.02	143	0.33	207	0.08	263	0.09
82	0.07	144	0.08	208	0.05	264	0.03
83	0.03	145	0.15	209	0.04	265	0.02
84	0.05	146	0.04	210	0.06	266	0.16
85	0.05	148	0.19	211	0.06	267	0.42
86	0.03	149	0.11	212	0.24	268	0.12
87				213	0.09	269	0.35

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
270	0.12	322	0.05	378	0.06	449	0.01
271	0.11	323	0.07	379	0.06	454	0.01
272	0.04	324	0.06	380	0.02	455	0.11
274	0.04	325	0.03	381	0.02	456	0.02
274	0.15	326	0.01	382	0.01	458	0.03
275	0.08	327	0.03	383	0.01	459	0.06
276	0.02	328	0.04	384	0.01	460	0.02
278	0.03	329	0.12	385	0.05	463	0.03
279	0.06	330	0.04	386	0.09	466	0.03
280	0.05	331	0.09	387	0.03	467	0.26
281	0.20	332	0.03	388	0.04	468	0.05
282	0.06	333	0.03	389	0.22	469	0.01
283	0.03	334	0.02	390	0.15	477	0.01
284	0.03	335	0.09	391	0.03	478	0.03
285	0.19	336	0.24	393	0.03	479	0.01
286	0.15	337	0.22	397	0.47	481	0.01
287	0.10	338	0.08	396	0.16	485	0.80
288	0.06	339	0.58	399	0.02	486	0.13
289	0.18	340	0.25	400	0.01	487	0.05
290	0.14	341	0.07	402	0.01	488	0.01
291	0.07	342	0.02	407	0.02	491	0.01
292	0.04	343	0.15	408	0.18	497	0.01
293	0.37	344	0.03	409	0.11	505	0.12
294	0.09	345	0.01	410	0.04	506	0.03
295	0.02	347	1.04	411	0.01	507	0.01
296	0.02	348	0.34	413	0.06	508	0.01
297	0.08	349	0.07	414	0.01	509	0.01
298	0.22	350	0.05	415	0.02	516	0.03
299	0.07	351	0.04	416	0.28	517	0.05
300	0.16	352	0.04	417	0.55	518	0.01
301	0.13	353	0.02	418	0.11	527	0.07
302	0.07	355	0.02	419	0.02	528	0.05
303	0.03	357	0.07	420	0.01	529	0.02
304	0.10	358	0.13	421	0.01	535	0.09
305	0.10	359	0.04	422	0.01	536	0.10
306	0.03	360	0.02	427	0.01	537	0.02
307	0.03	361	0.02	428	0.02	555	1.28
308	0.06	362	0.02	429	0.05	556	0.28
309	0.31	363	0.01	430	0.01	557	0.04
310	0.10	364	0.01	431	0.03	566	0.01
311	0.05	365	0.04	435	0.06	567	0.01
312	0.13	366	1.11	436	0.62	577	0.01
313	0.04	367	0.91	437	0.13	585	0.02
314	0.02	368	0.16	438	0.02	586	0.02
315	0.02	369	0.07	439	0.03	605	0.07
316	0.43	370	0.04	440	0.03	606	0.01
317	0.25	371	0.05	441	0.01	655	0.03
318	0.09	372	0.02	443	0.01	656	0.01
319	0.18	374	0.01	446	0.01	674	0.07
320	0.12	375	0.01	447	0.10	675	0.02
321	0.15	377	0.02	448	0.04		

50) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile RMM 748 (71)



51) 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile RMM 493 (72)



Paul

PR115N 381 (6.351)

No	Mass	Inten	%BPI	%TIC	No	Mass	Inten	%BPI	%TIC
1:	35	2.06e3	0.71	0.25	43:	400	1.78e2	0.13	0.05
2:	37	7.92e2	0.27	0.10	44:	402	2.35e3	0.80	0.29
3:	42	1.57e2	0.06	0.02	45:	403	4.80e2	0.16	0.06
4:	79	1.97e3	0.83	0.23	46:	405	2.99e4	9.81	3.53
5:	81	1.76e3	0.60	0.21	47:	406	3.78e3	1.27	0.46
6:	176	8.64e2	0.29	0.11	48:	421	2.20e4	7.47	2.69
7:	286	4.40e2	0.15	0.05	49:	422	1.20e3	0.41	0.15
8:	305	1.10e3	0.37	0.13	50:	424	2.66e5	90.28	32.49
9:	306	2.31e2	0.08	0.03	51:	425	3.87e4	13.11	4.72
10:	312	1.52e3	0.52	0.19	52:	426	8.26e2	0.28	0.10
11:	317	1.06e3	0.36	0.13	53:	433	7.38e2	0.25	0.09
12:	321	7.56e2	0.26	0.09	54:	437	4.60e2	0.16	0.06
13:	324	8.13e3	2.76	0.99	55:	440	4.52e2	0.15	0.06
14:	325	1.30e3	0.44	0.16	56:	443	8.72e2	0.30	0.11
15:	331	3.44e2	0.12	0.04	57:	449	5.88e2	0.20	0.07
16:	333	4.87e3	1.58	0.57	58:	450	4.80e2	0.16	0.06
17:	334	6.56e2	0.22	0.08	59:	455	2.20e4	7.47	2.69
18:	336	3.54e3	1.30	0.47	60:	456	2.96e3	1.00	0.36
19:	337	5.76e2	0.20	0.07	61:	459	6.92e2	0.23	0.08
20:	343	6.24e2	0.21	0.08	62:	471	1.17e4	3.97	1.43
21:	349	5.00e2	0.17	0.06	63:	472	1.62e3	0.55	0.20
22:	350	3.92e2	0.13	0.05	64:	474	1.07e3	0.36	0.13
23:	352	1.15e3	0.39	0.14	65:	493	2.95e5	100.00	35.99
24:	353	3.80e2	0.13	0.05	66:	494	4.66e4	15.80	5.69
25:	355	6.98e3	2.37	0.85	67:	495	3.23e3	1.10	0.39
26:	356	5.12e2	0.17	0.06	68:	509	6.38e2	0.23	0.08
27:	359	1.78e3	0.60	0.22	69:	512	8.56e2	0.29	0.10
28:	361	6.16e2	0.21	0.08	70:	519	5.48e2	0.19	0.07
29:	362	1.06e3	0.36	0.13					
30:	367	8.36e2	0.29	0.10					
31:	369	3.68e2	0.12	0.04					
32:	371	8.32e3	2.92	1.02					
33:	372	1.09e3	0.37	0.13					
34:	374	2.22e3	0.75	0.27					
35:	375	3.52e2	0.12	0.04					
36:	381	3.56e2	0.12	0.04					
37:	383	1.17e3	0.40	0.14					
38:	386	1.70e3	0.58	0.21					
39:	387	3.60e2	0.13	0.05					
40:	390	1.17e2	0.05	0.02					
41:	398	3.92e2	0.13	0.05					
42:	399	6.00e2	0.20	0.07					

Appendix C IR Spectroscopy.

Chapter II

1) 6-(tert-butyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(7)**
2) 2,6-bis(tert-butyl)-3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(8)**
3) 4-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-pyridyl}heptane-3,5-dione **(9)**
4) 6-(prop-1-enyl)-2,3,5-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(10)**
5) 2,3,5-trifluoro-6-phenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine **(11)**
6) 3,5-difluoro-2,6-diphenyl-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl]pyridine **(12)**
7) 2,3,5-trifluoro-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(13)**
8) 2,5-difluoro-3,6-diprop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(14)**
9) 3,5-difluoro-2-methoxy-6-prop-1-ynyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyridine **(15)**
10) diethyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine **(18)**
11) {6-(diethylamino)-3,5-difluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}diethylamine **(19)**
12) benzyl{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-trifluoromethyl)ethyl](2-pyridyl)}amine **(20)**

Chapter III

13) 19,20-diaza-8,17-bis[1,2,2,2-tetrafluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11,14-tetraoxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene **(35)**

14) 25,26-diaza-11,23-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-10,12,22,24-tetrafluoro-2,5,8,14,17,20-hexaoxatricyclo[19.3.1.1,9,13.]hexacosa-1(25),9,11,13(26),21,23-hexaene **(37)**

15) 26,28-diaza-5,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-4,6,16,18-tetrafluoro-11,23-dimethyl-2,8,14,20-tetraoxapentacyclo[19.3.1.1<3,7>.1<9,13>.1<15,19>]octacosa-1(24),3,5,7(26),9,(27),10,12,15,17,19(28),21(25),22-dodecaene **(39)**

16) 11,14,19,20-tetraaza-8-17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-11,14-dimethyl-2,5-dioxatricyclo-[13.3.1.1,6,10.]icosa-1(19),6,8,10,(20),15,17-hexaene **(42)**

17) 2,5,22,23-tetraaza-8,20-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,19,21-tetrafluoro-2,5-dimethyl-11,14,17-trioxatricyclo[16.3.1.1<6,10>]-tricosa-1(22),6,8,10(23),18,20-hexaene **(43)**

18) 14,19,20-triaza-8,17-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-7,9,16,18-tetrafluoro-2,5,11-trioxatricyclo[13.3.1.1<6,10>]icosa-1(19),6,8,10(20),15,17-hexaene **(45)**

19) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine **(46)**

20) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-(2,3,5,6-tetrafluoro(4-pyridyloxy))octane **(47)**

21) methyl(2-{methyl[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl]amino}ethyl)[3,5,6-trifluoro-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)(2-pyridyl)]amine **(48)**

22) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane **(49)**

Chapter IV

23) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,5-difluoropyrimidine **(50)**

24) 2,5-difluoro-4-methoxy-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine **(52)**

25) 5-fluoro-2,6-dimethoxy-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine **(53)**

26) 6-(2-{2,5-difluoro-1-(trifluoromethyl)ethyl]pyrimidin-4-yloxy}ethoxy)-2,5-difluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]pyrimidine **(54)**

27) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoro-1-(trifluoromethyl)ethyl]-5-fluoro-2-methoxypyrimidine **(55)**

28) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-dodecyloxy-5-fluoropyrimidine **(56)**

29) 4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2-({4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}ethoxy)-5-fluoropyrimidine **(57)**

30) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}diethylamine **(58)**

31) {4,6-bis[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-5-fluoropyrimidin-2-yl}benzylamine **(59)**

32) 2,5,6-trifluoro-4-methoxypyrimidine **(60)**

33) 2,5-difluoro-6-hydroxy-4-methoxypyrimidine **(61)**

34) 6-[2-(2,5-difluoro-6-methoxypyrimidin-4-yloxy)ethoxy]-2,5-difluoro-4-methoxypyrimidine **(62)**

Chapter V

35) 3,5,6-trifluoro-2-phenoxy-4-trifluoromethylpyridine **(65)**

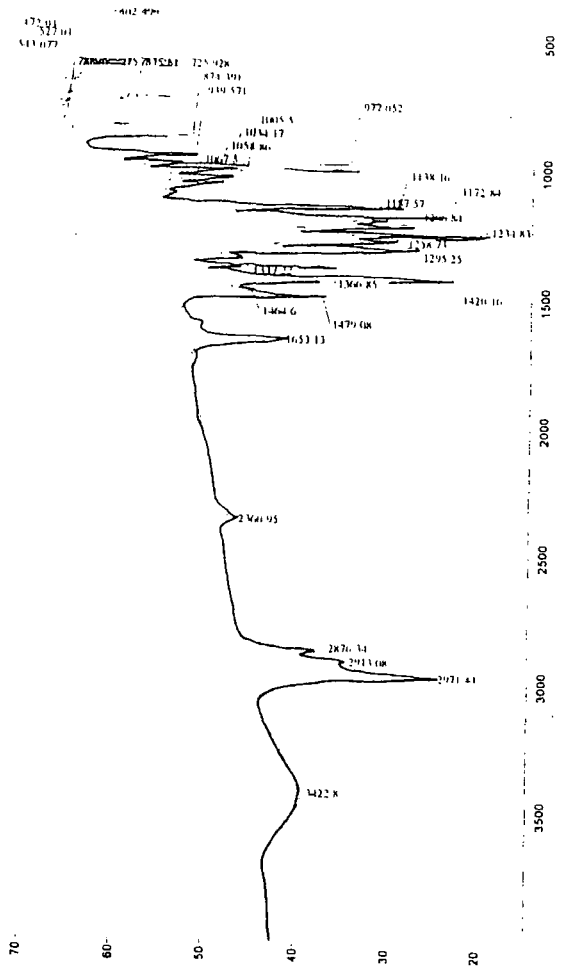
36) 2,3,5,6-tetrafluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]pyridine **(66)**

37) (1R,2S)-2-methyl{3,5,6-trifluoro-4-[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl](2-pyridyl}amino)-1-phenylpropan-1-ol **(67)**

38) 4,6-bis[1,2,2,3,3,3-hexafluoro-1-(trifluoromethyl)propyl]-3,5-difluorobenzene-1,2-dicarbonitrile **(69)**

39) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-6-fluoro-3-phenoxybenzene-1,2-dicarbonitrile **(70)**

40) 4,5-bis[1,2,2,3,3,3-hexafluoro-1-trifluoromethyl)propyl]-3,6-diphenoxybenzene-1,2-dicarbonitrile **(71)**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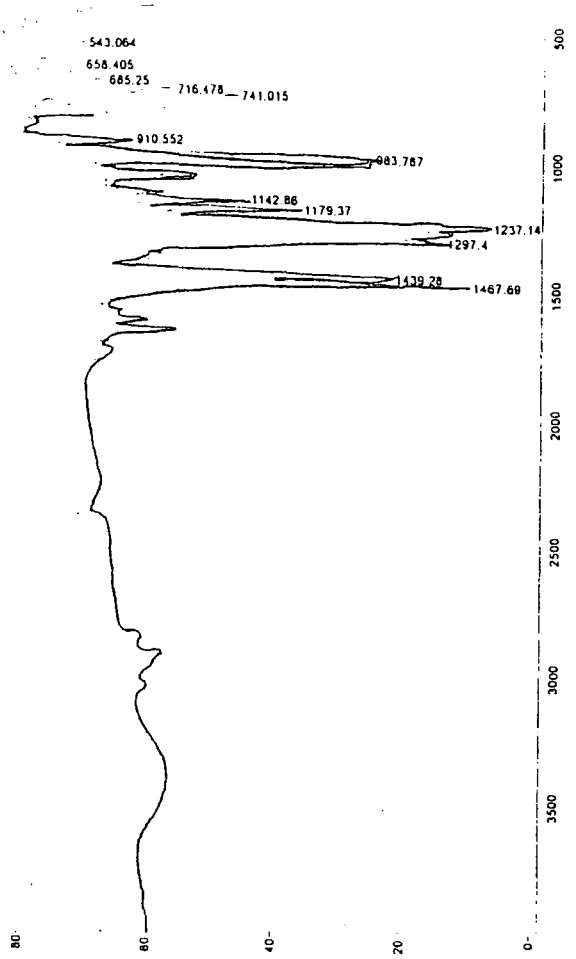
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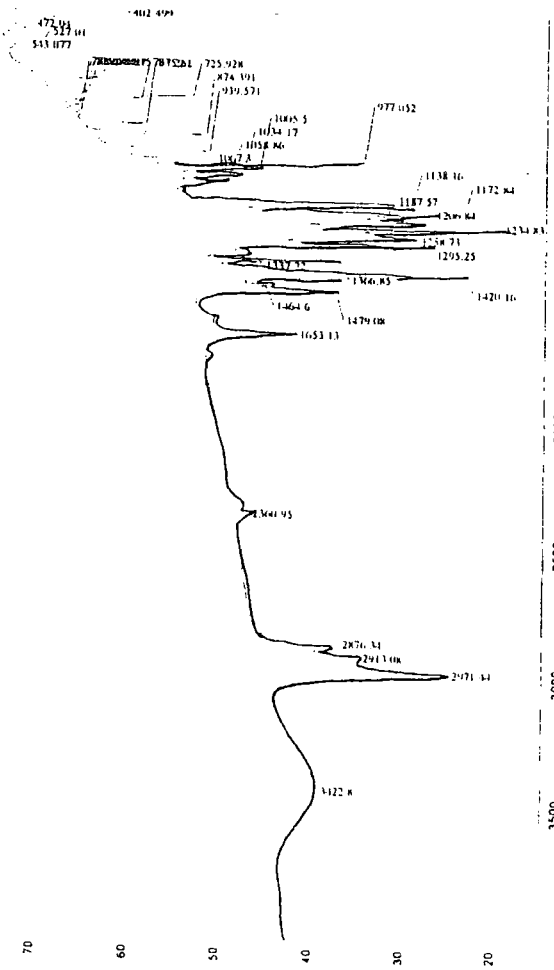
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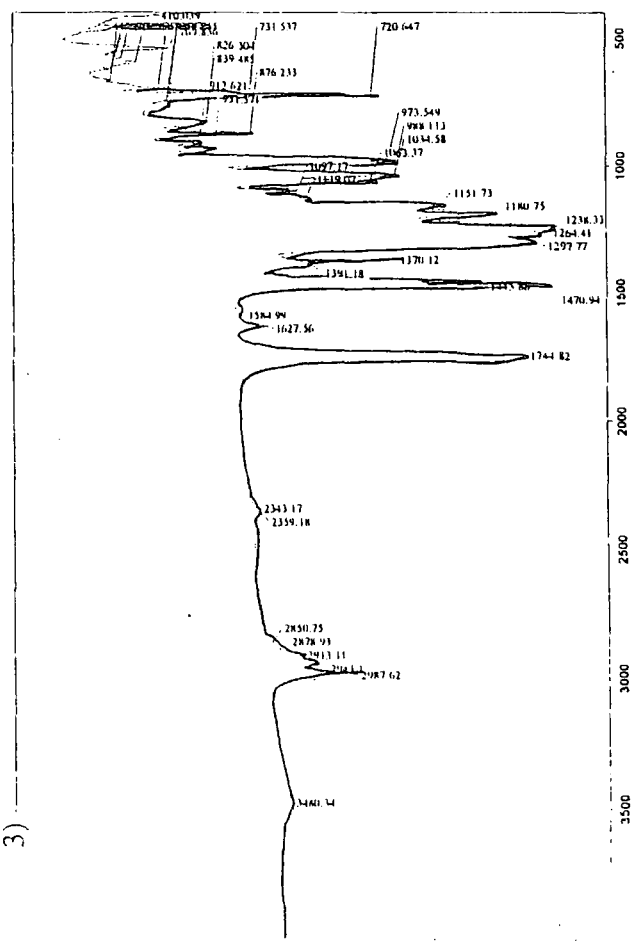
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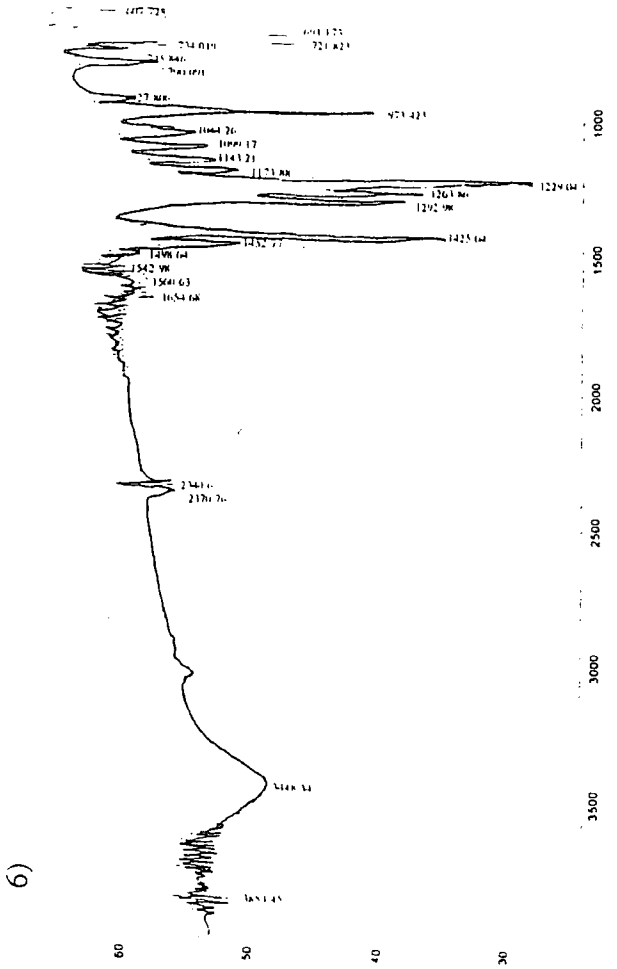
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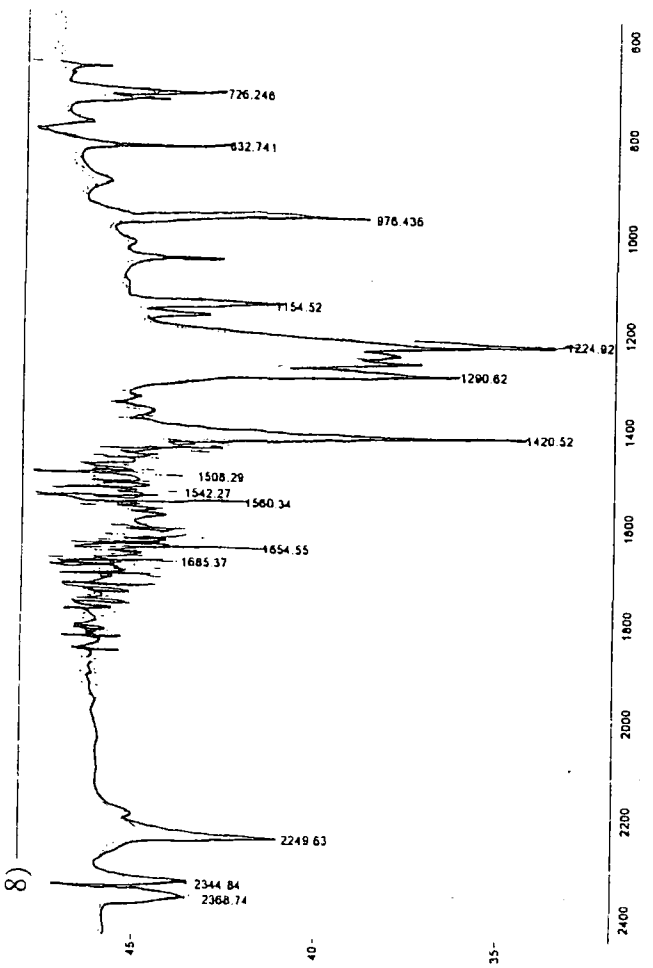
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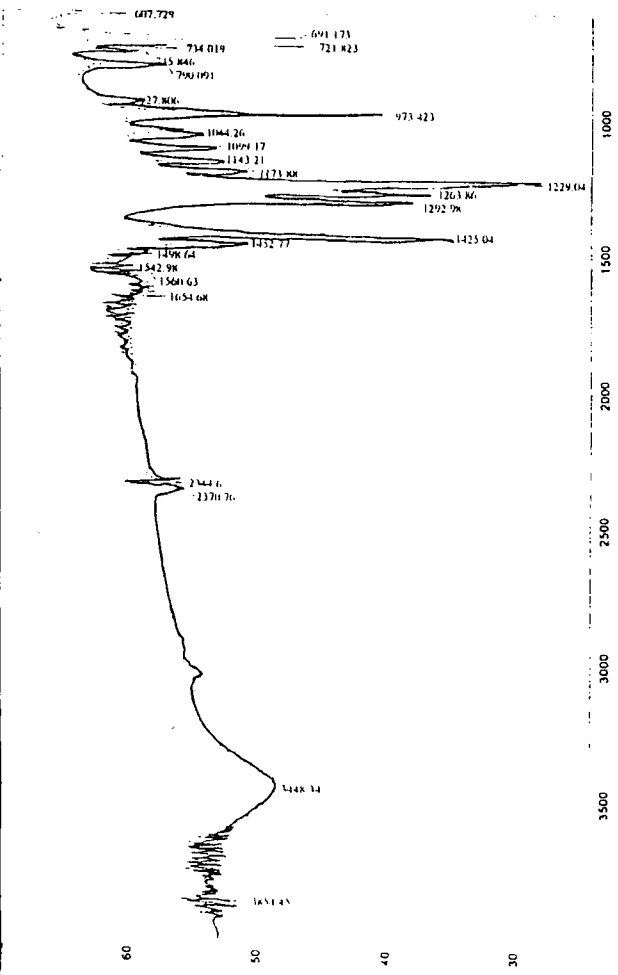
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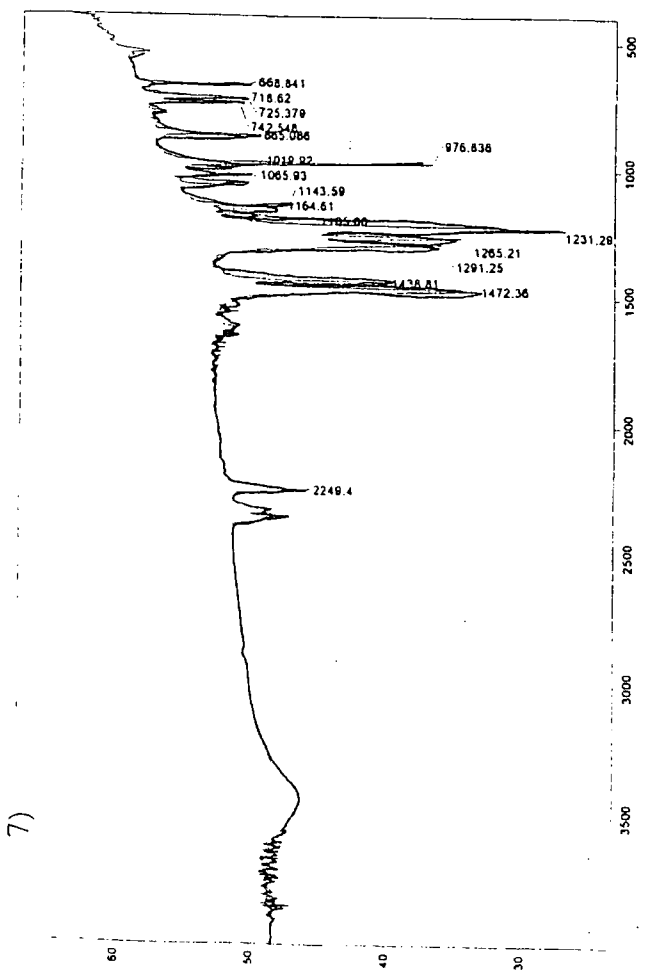
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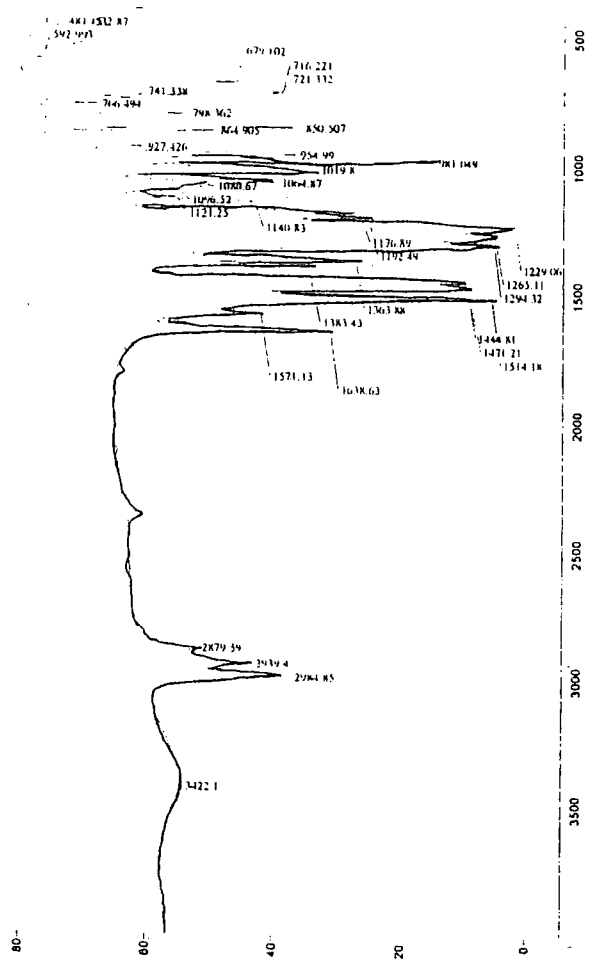

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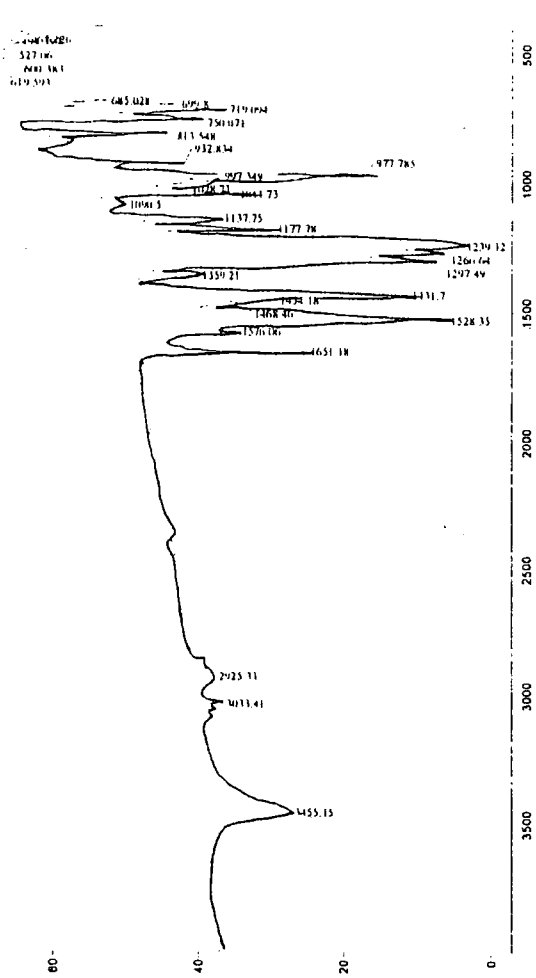

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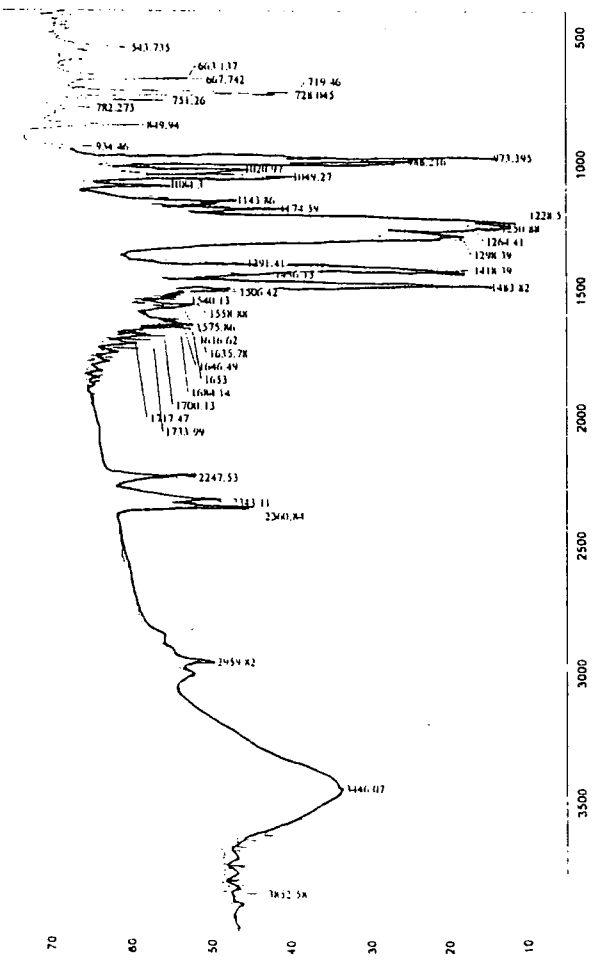

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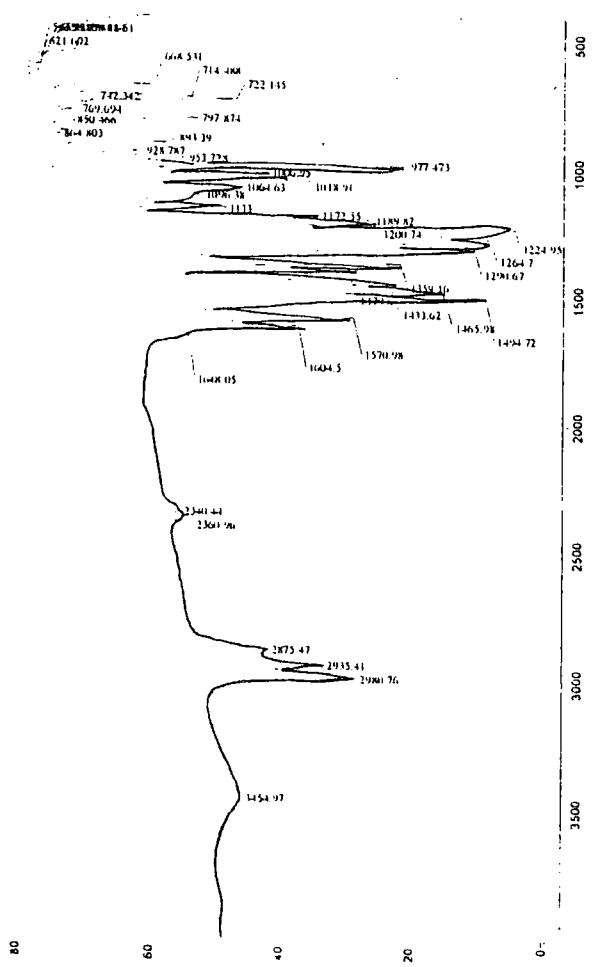

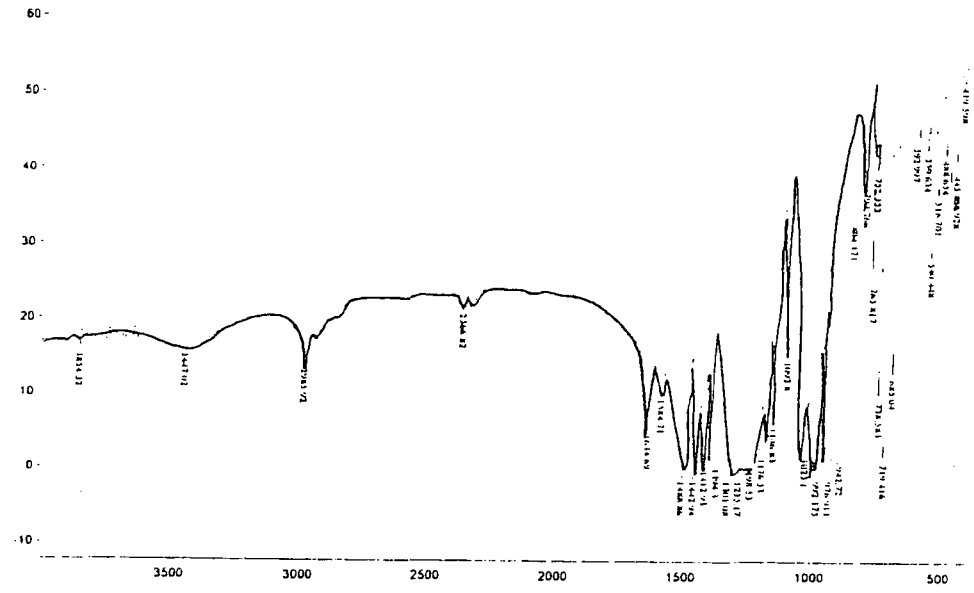
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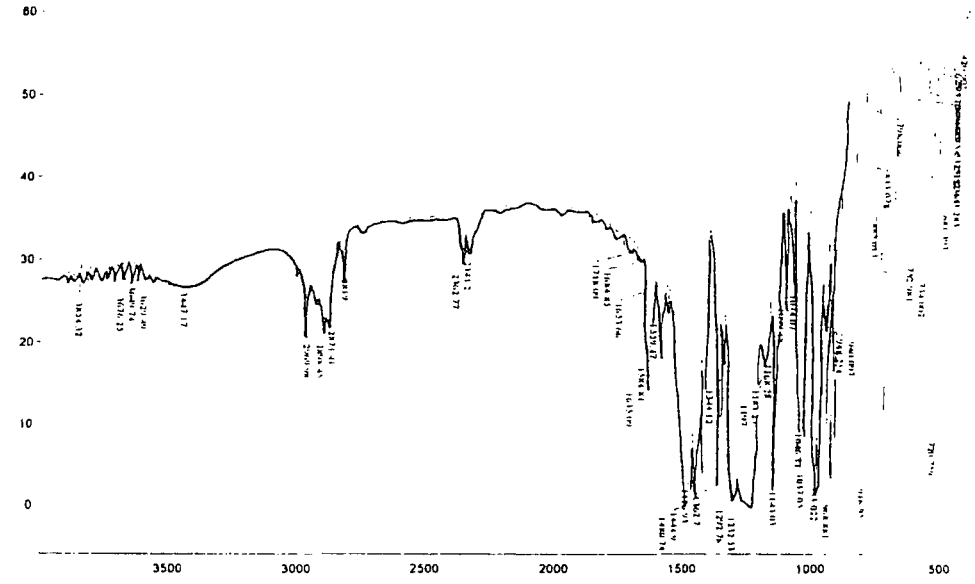
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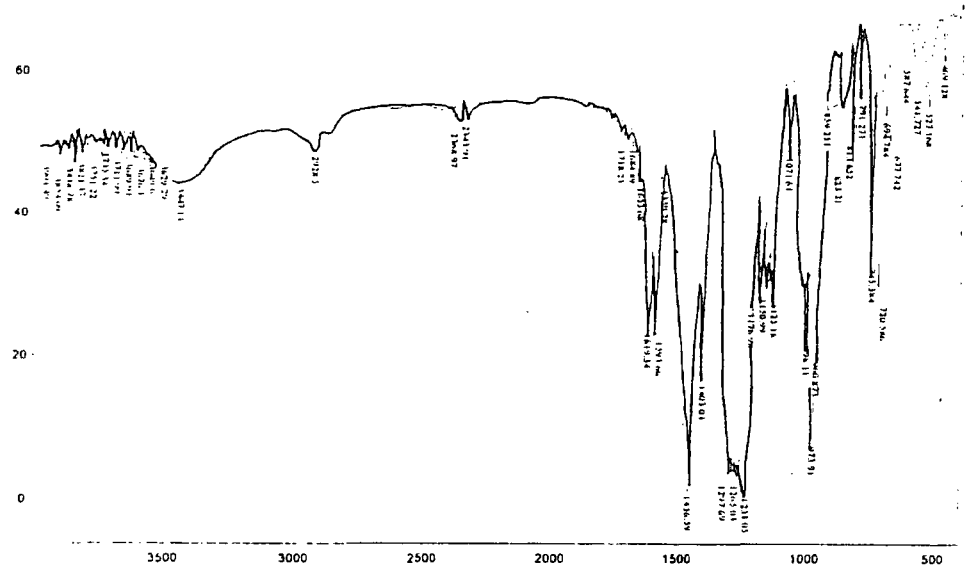
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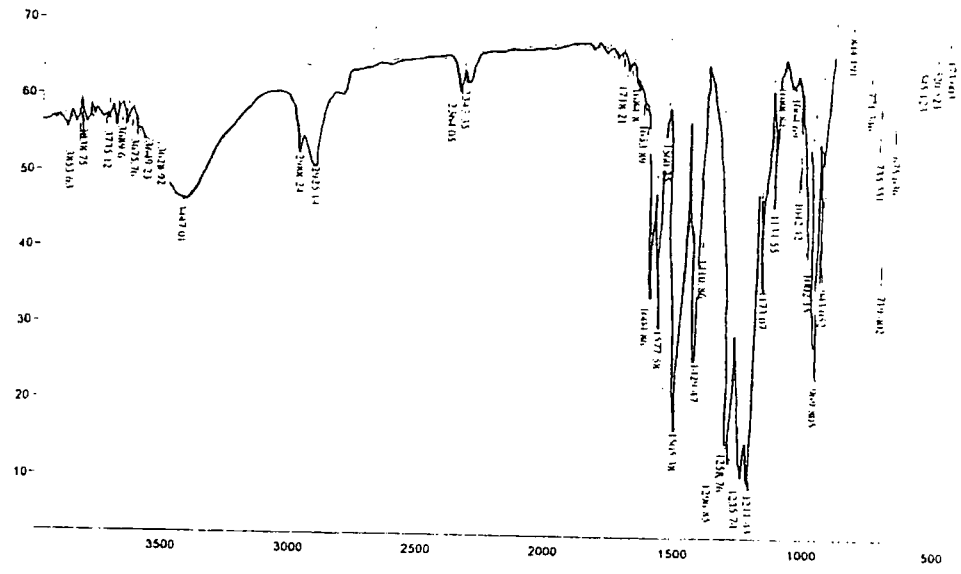
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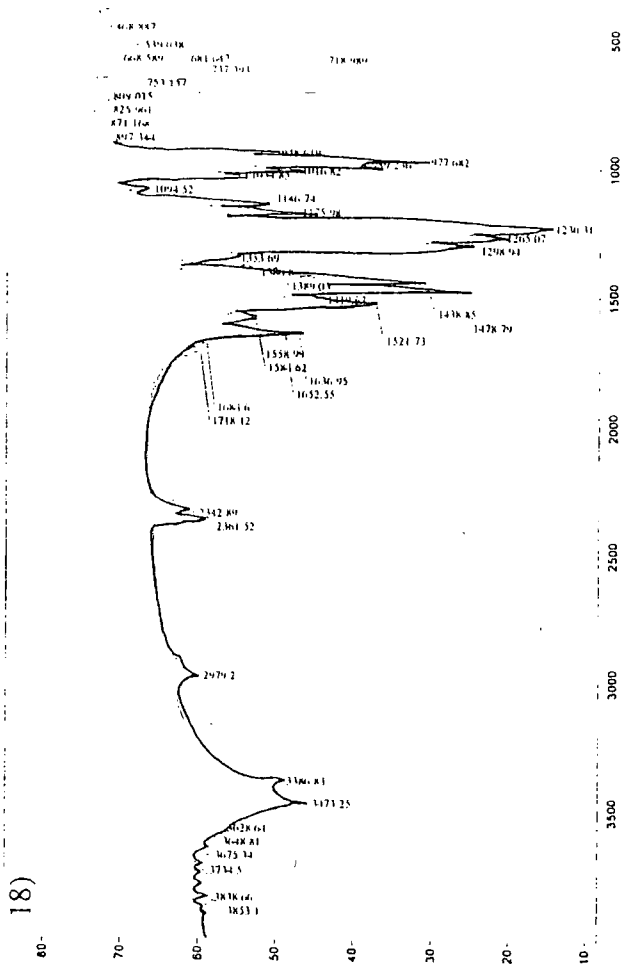
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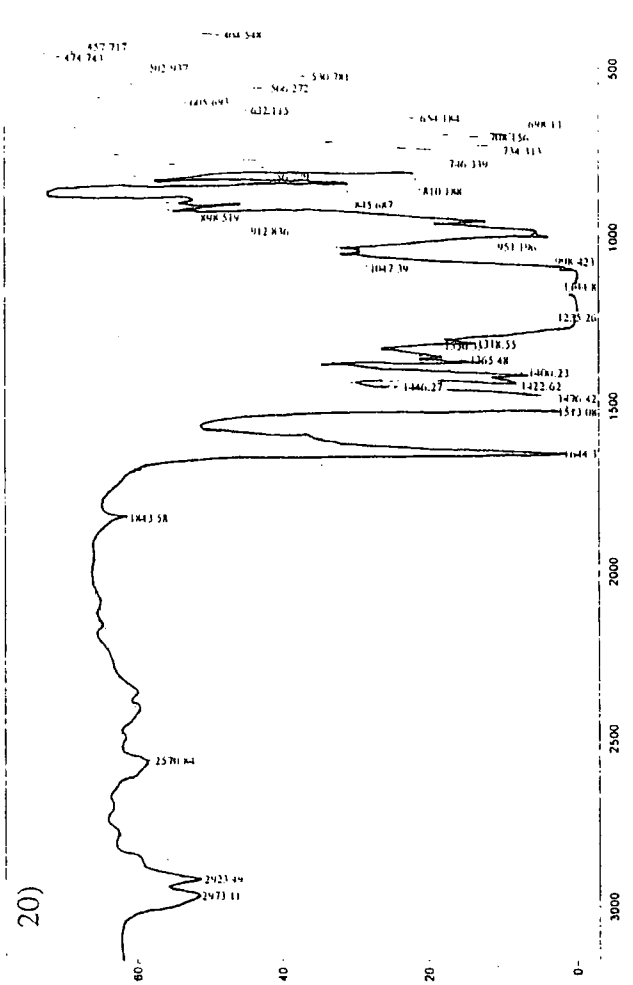
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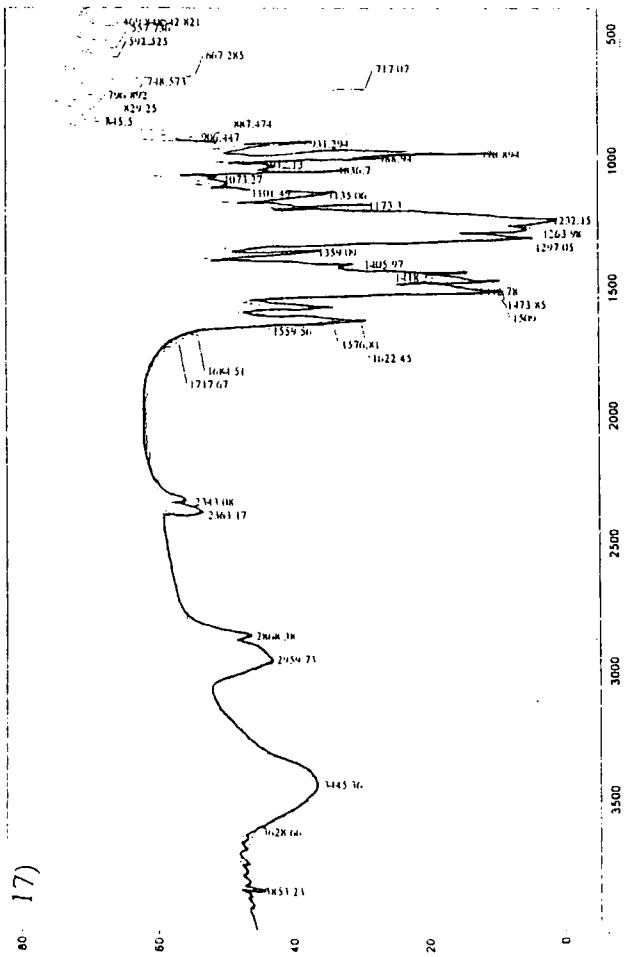
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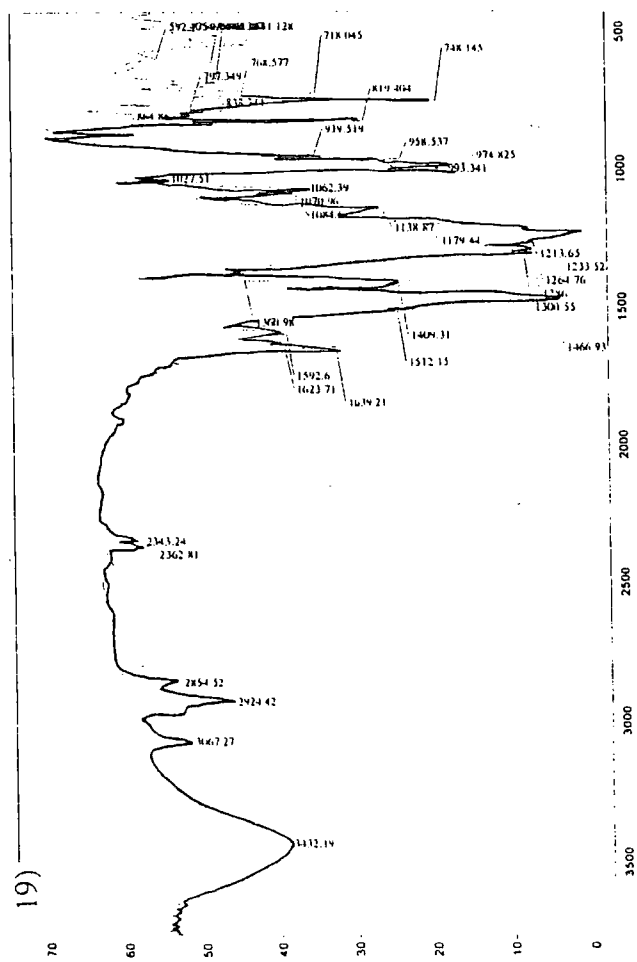
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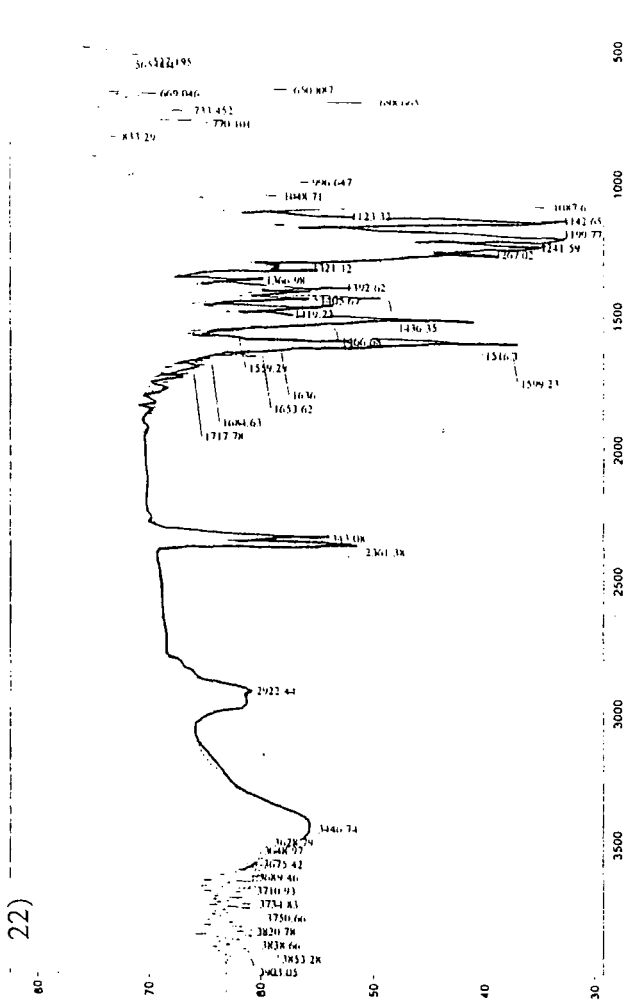

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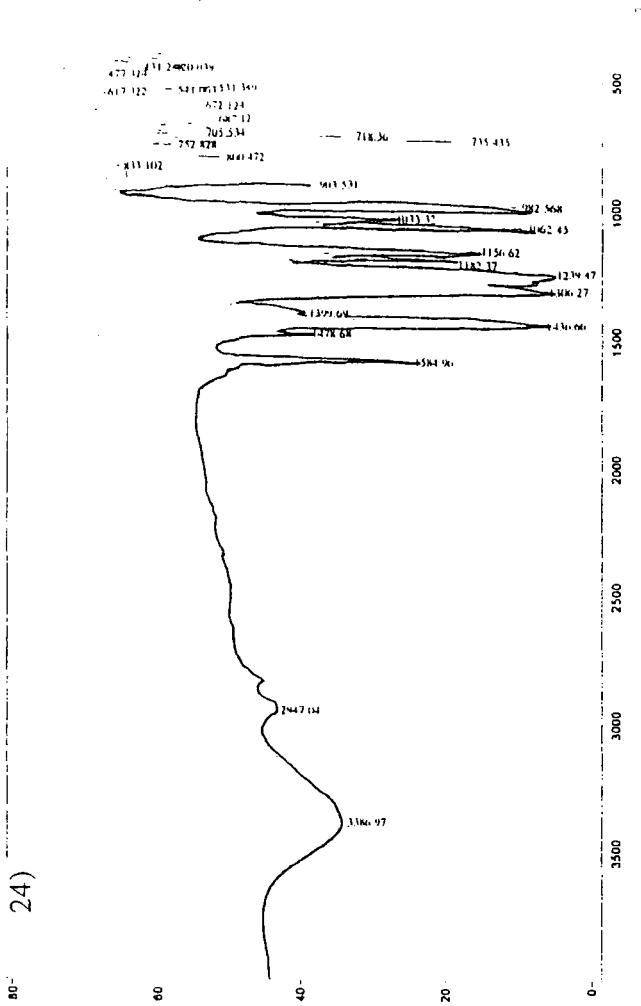

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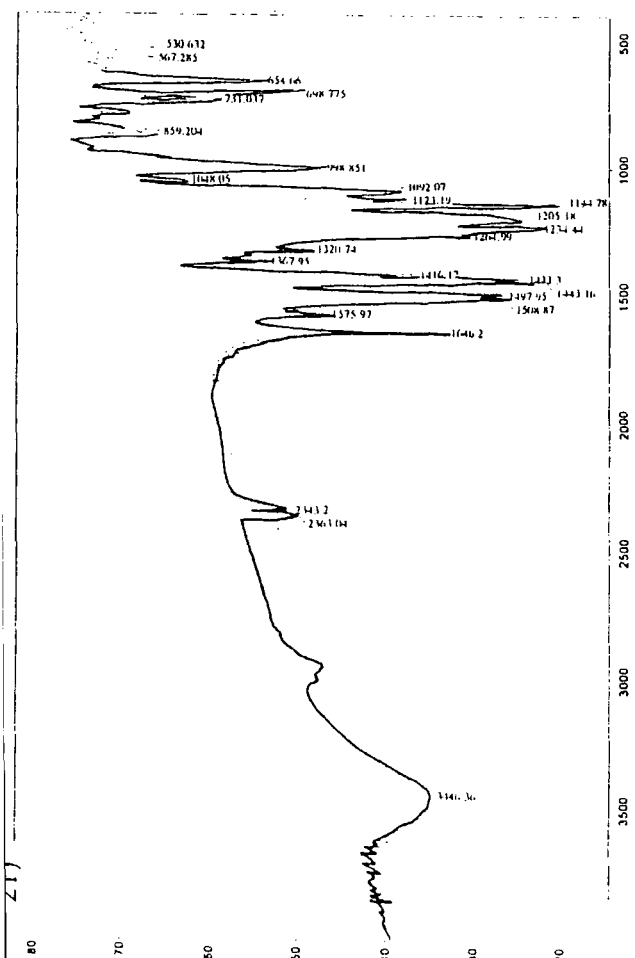

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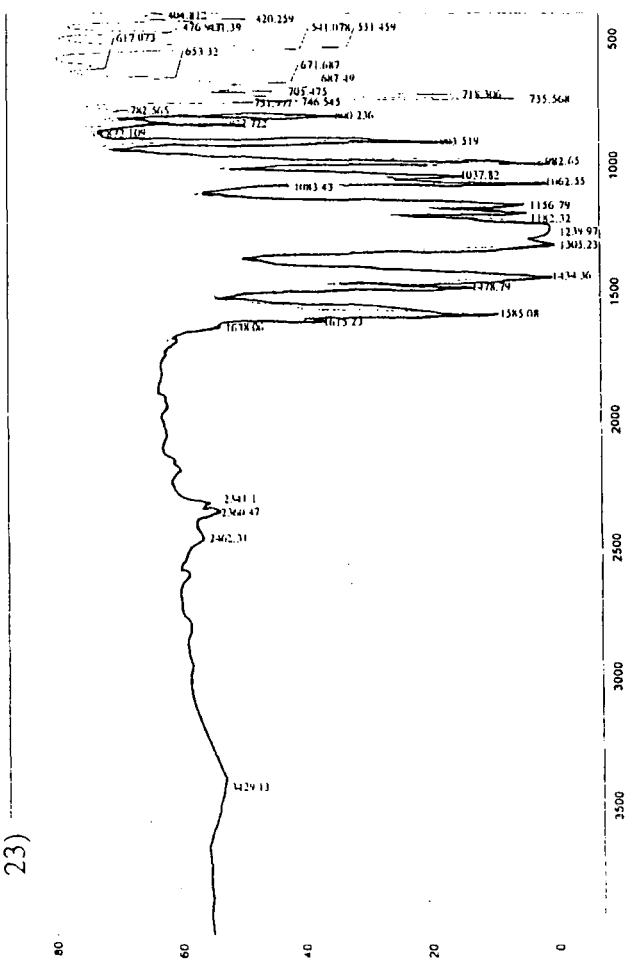

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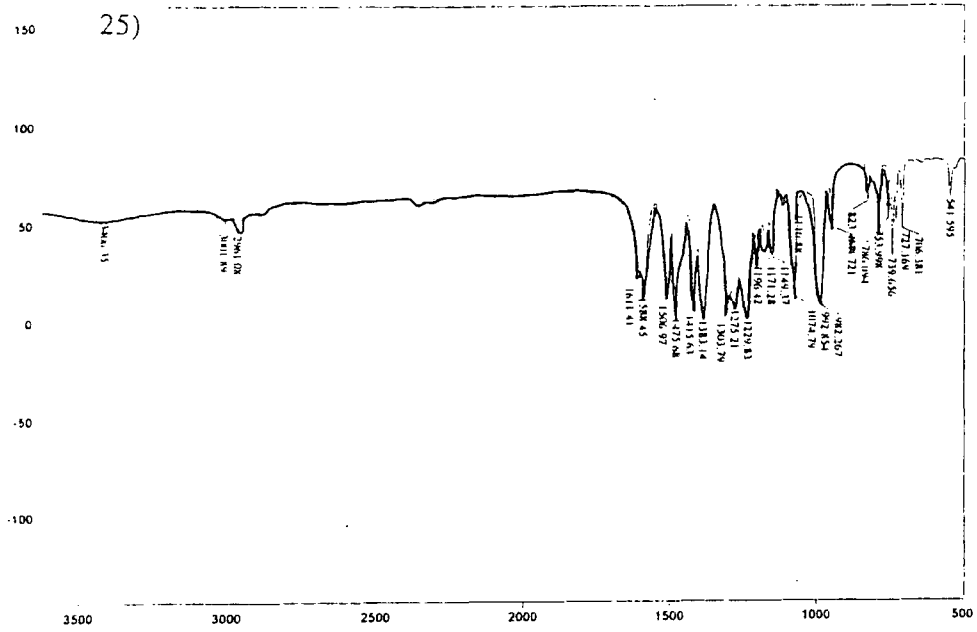

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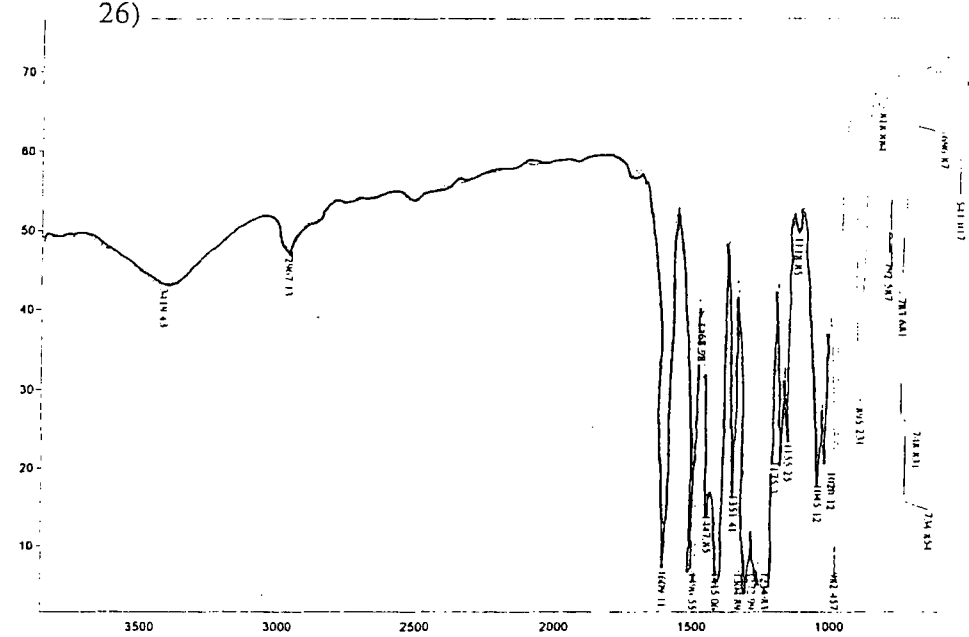

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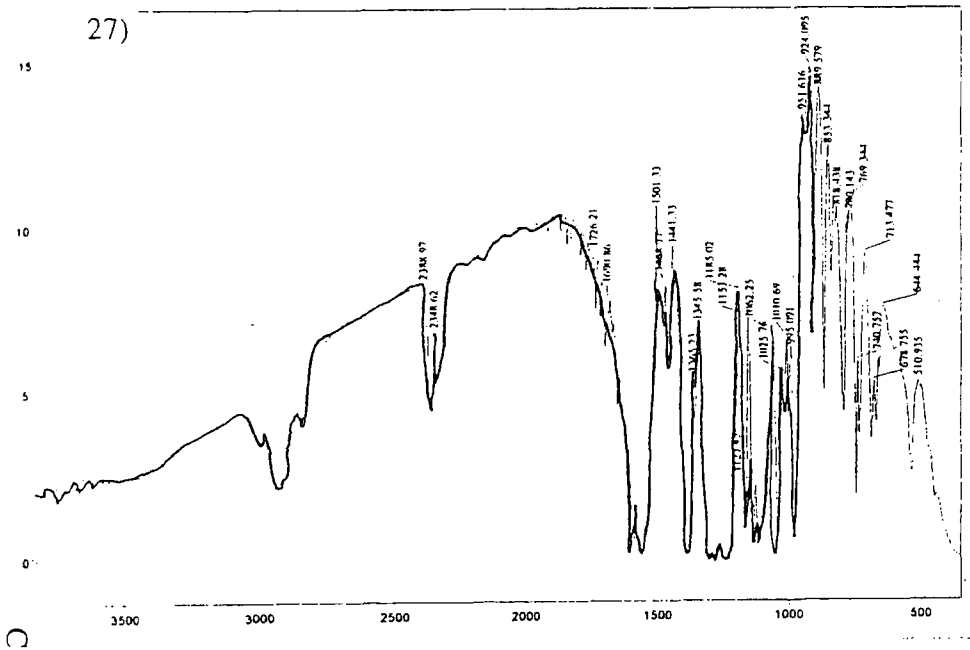

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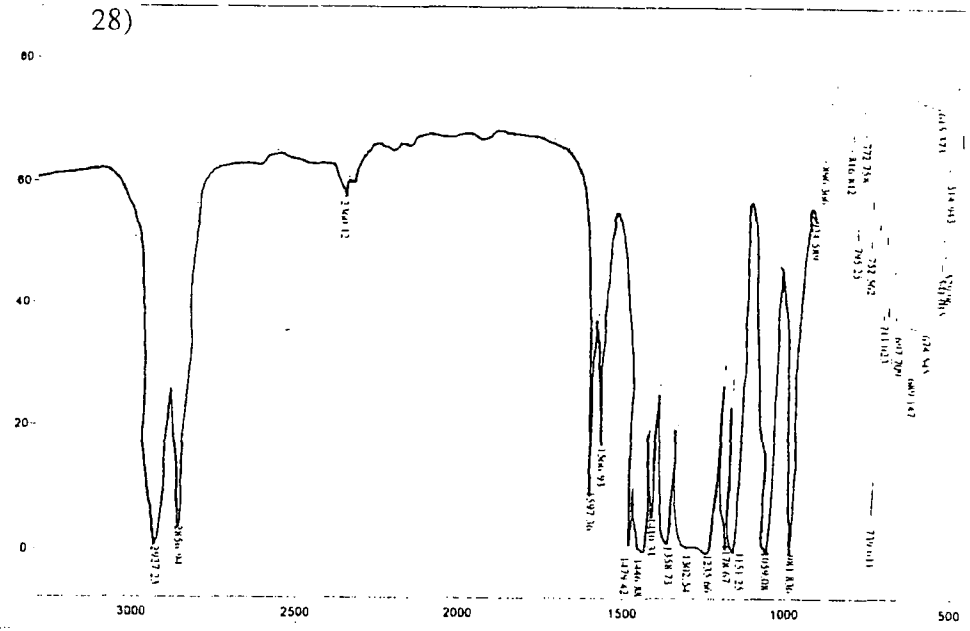
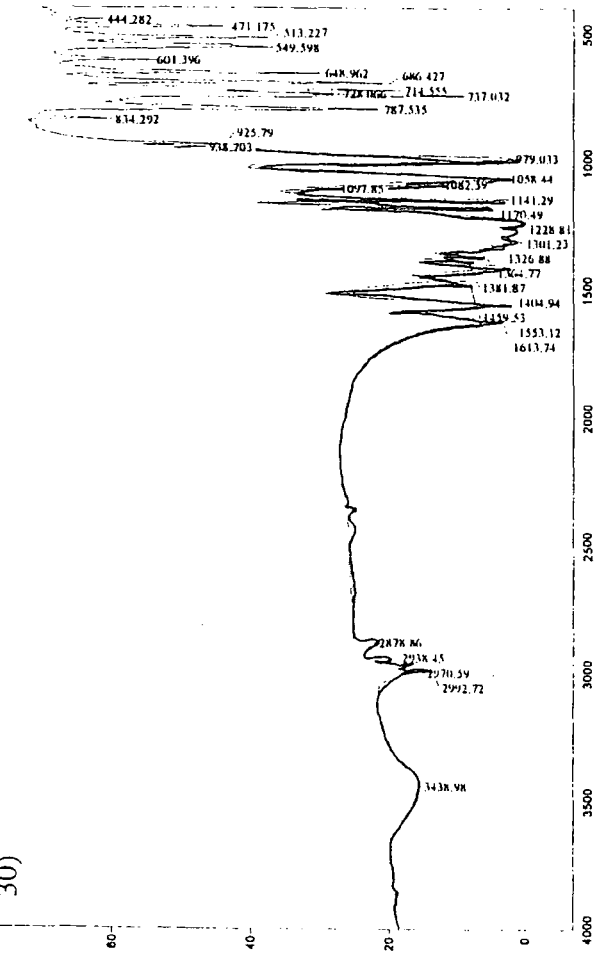


C12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1082.39
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1228.81
1301.23
1326.88
1361.87
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1613.74
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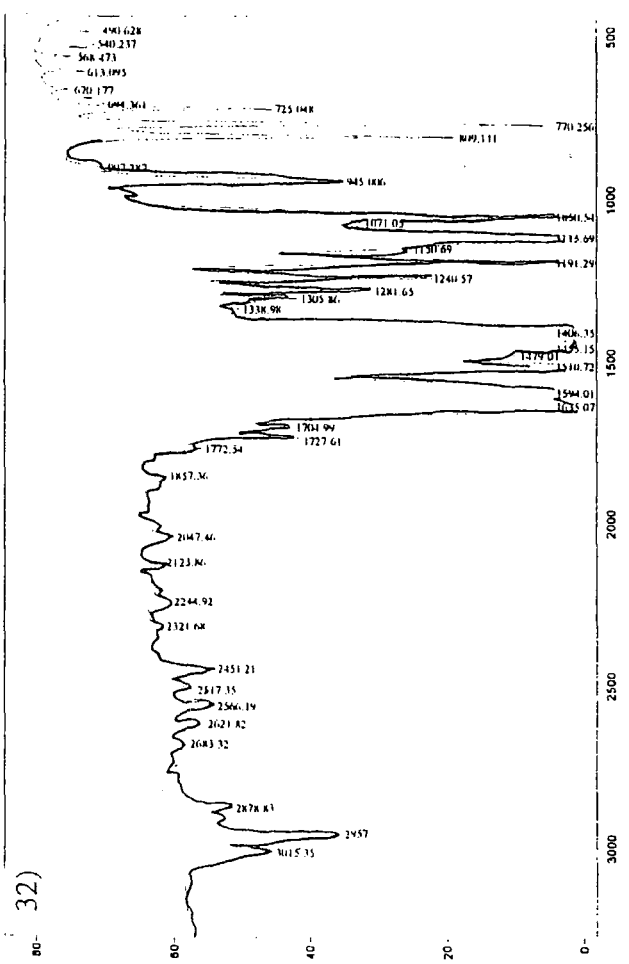
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1305.86
1338.98
1406.35
1510.72
1594.01
1635.07
1704.99
1727.61
1772.54
1857.36
2147.46
2123.86
2244.92
2321.68
2451.21
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2566.19
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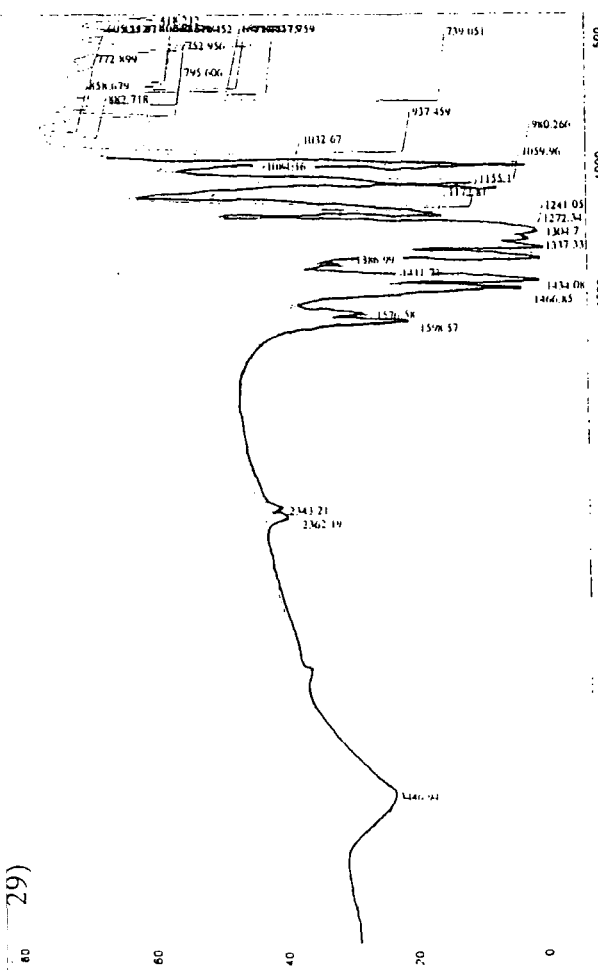
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1303.7
1317.33
1434.08
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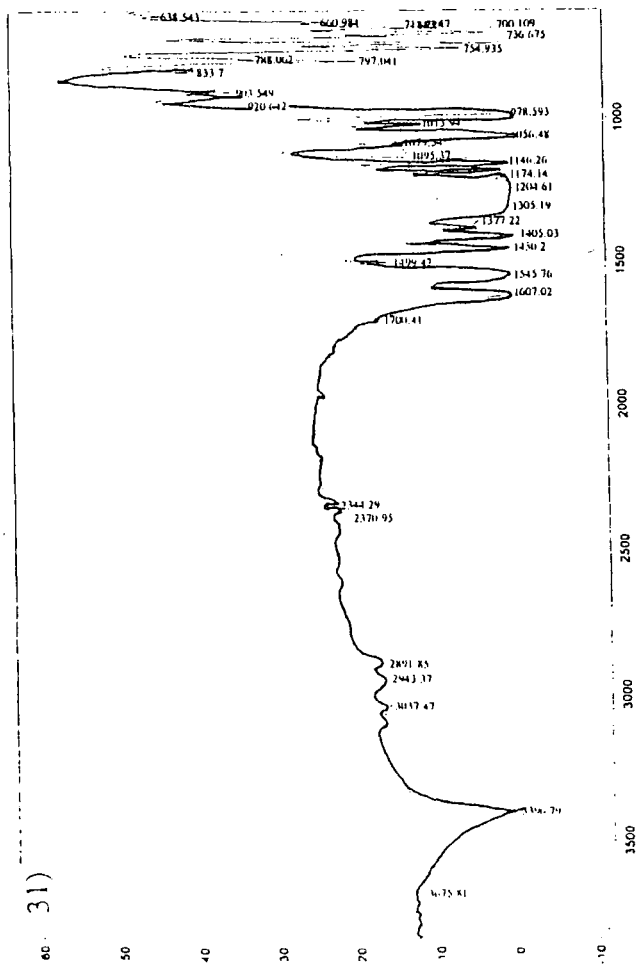
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1377.22
1405.03
1430.2
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1607.02
1701.41
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2370.95
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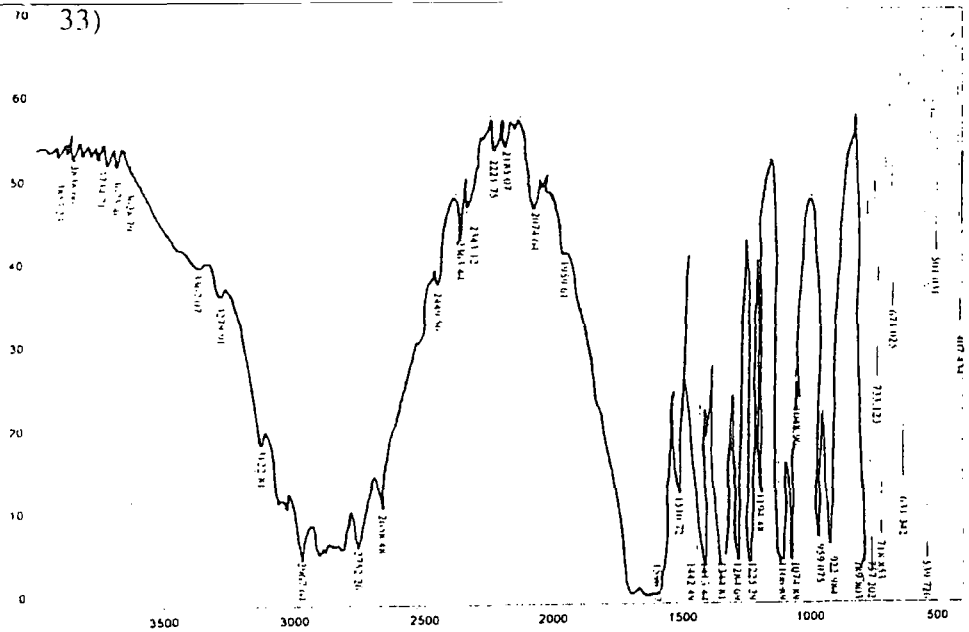
31)

33)



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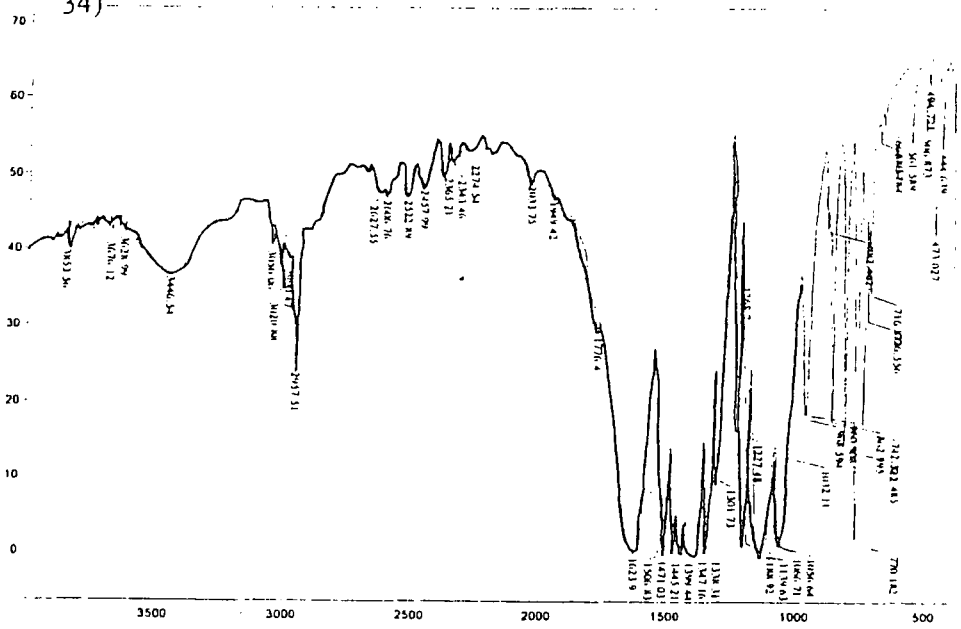

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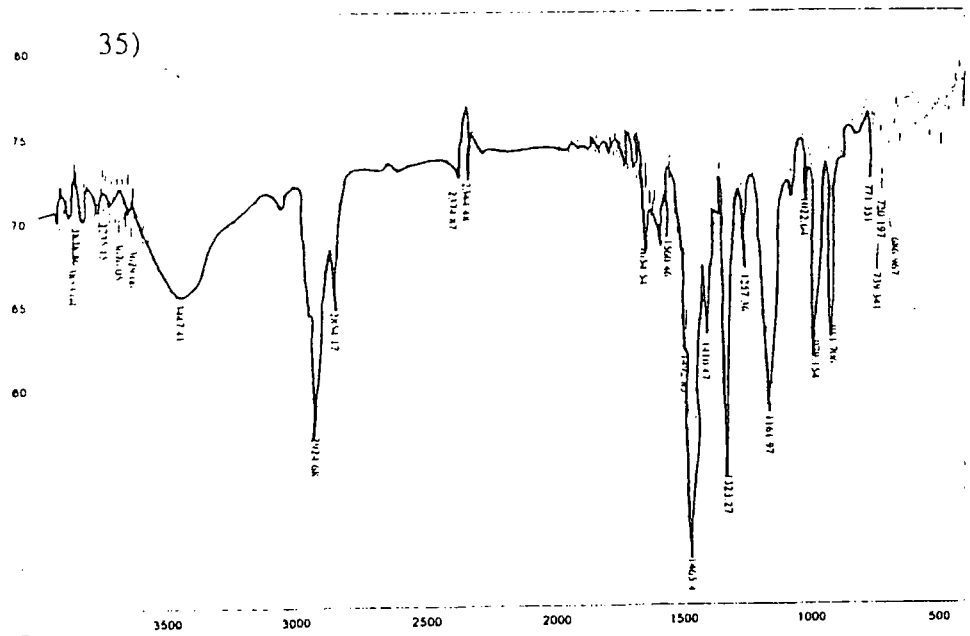

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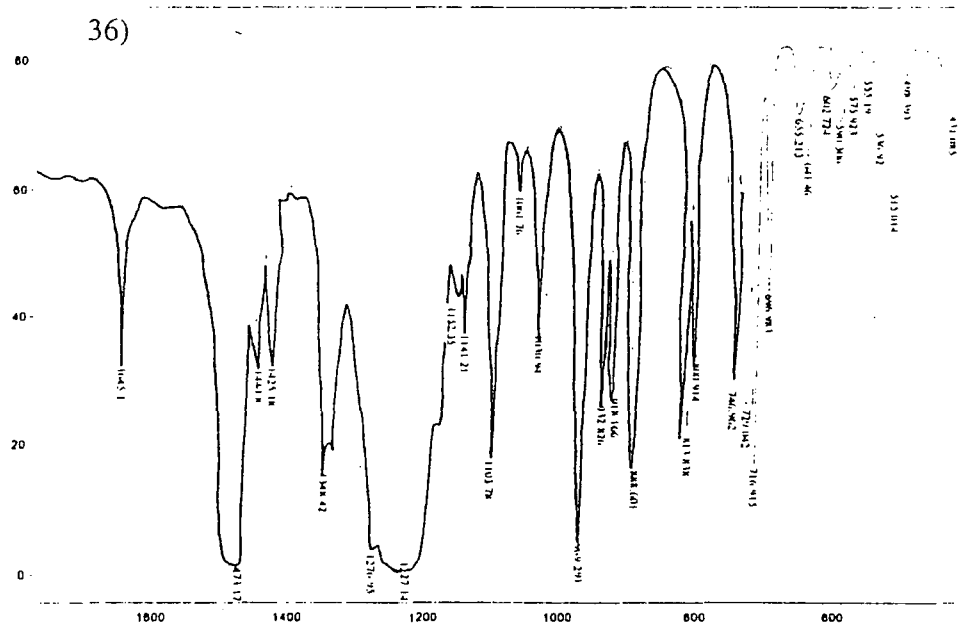

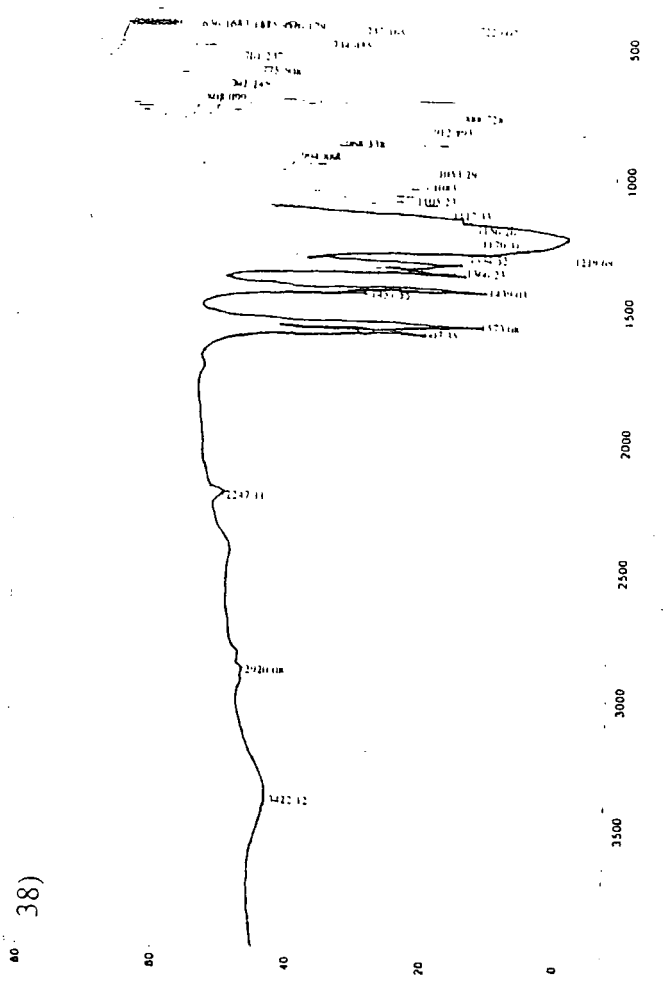

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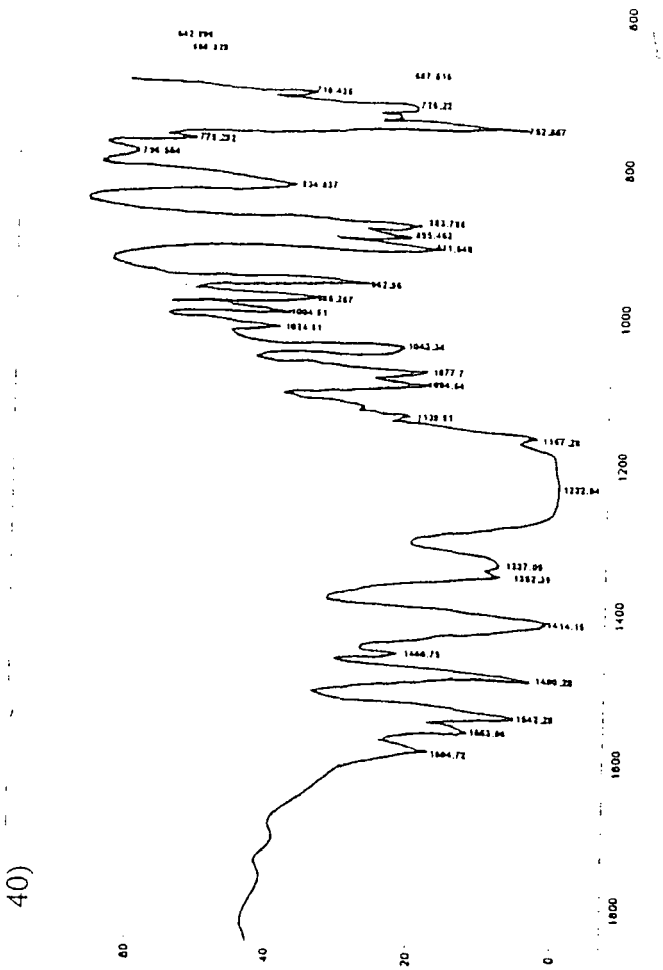
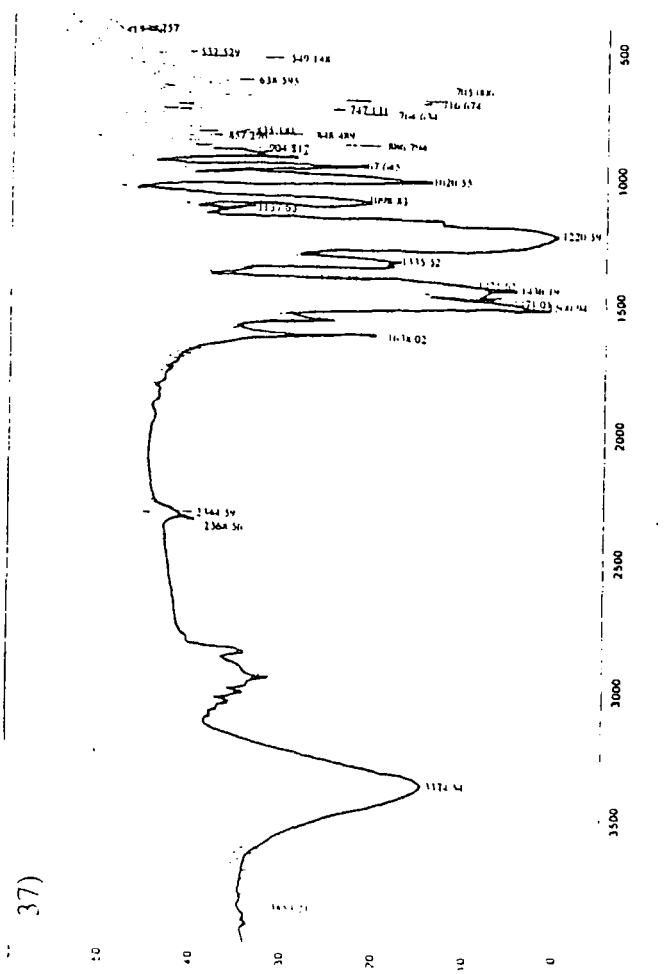


40)



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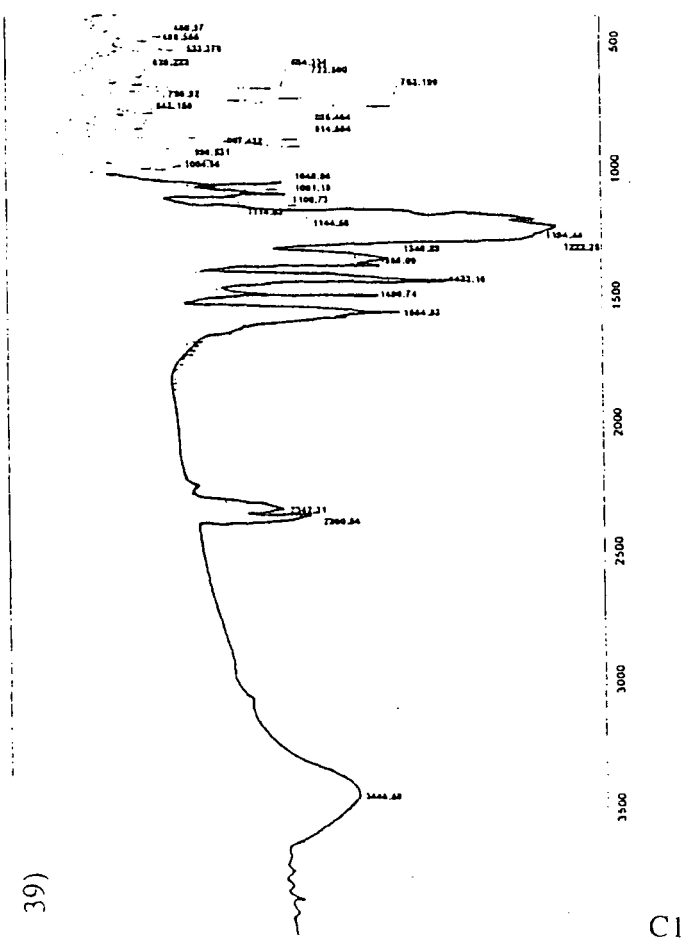

39)

Appendix D X-Ray Crystal Structure Data.

Chapter III

1) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine **(46)**

2) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane **(49)**

Chapter V

3) 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile **(72)**

1) 3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethylethyl]-2-[1-(2-{3,5,6-trifluoro-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl](2-pyridyloxy)}naphthyl)(2-naphthyloxy)pyridine (46)

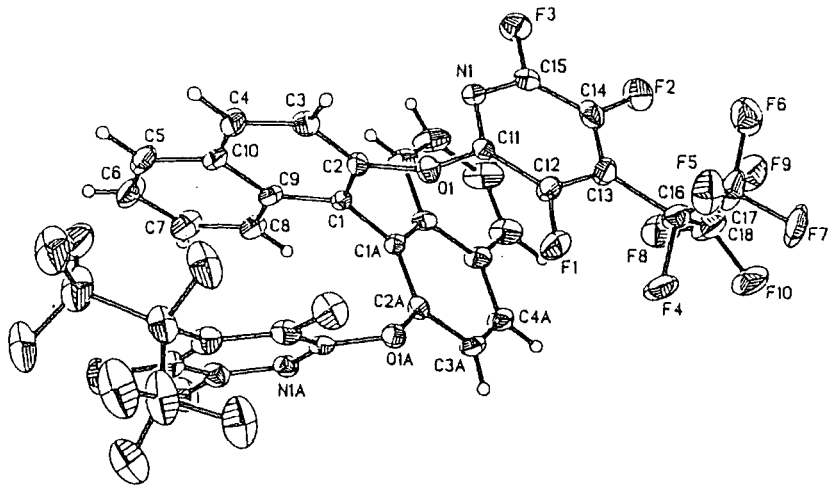

Table 1. Crystal data and structure refinement for 01srv017.

Identification code	s17s	
Empirical formula	$C_{36}H_{12}F_{20}N_2O_2$	
Formula weight	884.48	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 28.710(2) Å	α= 90°.
	b = 10.4001(6) Å	β= 114.605(2)°.
	c = 12.5791(7) Å	γ = 90°.
Volume	3414.9(3) Å^3	
Z	4	
Density (calculated)	1.720 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	1752	
Crystal size	0.26 x 0.26 x 0.13 mm^3	
Theta range for data collection	1.56 to 27.50°.	
Index ranges	-37<=h<=36, -13<=k<=13, -16<=l<=16	
Reflections collected	17731	
Independent reflections	3932 [R(int) = 0.0976]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9767 and 0.9542	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3932 / 3 / 327	
Goodness-of-fit on F^2	1.082	
Final R indices [I>2sigma(I)]	R1 = 0.0668, wR2 = 0.1665	
R indices (all data)	R1 = 0.0959, wR2 = 0.1818	
Largest diff. peak and hole	0.678 and -0.396 e.Å^{-3}	

Table 3. Bond lengths [Å] and angles [°] for 01srv017.

O(1)-C(11)	1.356(3)	F(8)-C(18)	1.339(6)	C(6)-C(7)	1.414(5)
O(1)-C(2)	1.412(3)	F(9)-C(18)	1.350(5)	C(7)-C(8)	1.373(4)
N(1)-C(15)	1.308(4)	F(10)-C(18)	1.314(5)	C(8)-C(9)	1.418(4)
N(1)-C(11)	1.319(4)	C(1)-C(2)	1.369(4)	C(9)-C(10)	1.428(4)
F(1)-C(12)	1.344(3)	C(1)-C(9)	1.440(4)	C(11)-C(12)	1.395(4)
F(2)-C(14)	1.333(3)	C(1)-C(1)#1	1.496(5)	C(12)-C(13)	1.392(4)
F(3)-C(15)	1.330(3)	C(2)-C(3)	1.401(4)	C(13)-C(14)	1.386(5)
F(4)-C(16)	1.389(4)	C(3)-C(4)	1.368(4)	C(13)-C(16)	1.544(4)
F(5)-C(17)	1.329(4)	C(4)-C(10)	1.413(4)	C(14)-C(15)	1.392(4)
F(6)-C(17)	1.372(5)	C(5)-C(6)	1.355(5)	C(16)-C(17)	1.495(6)
F(7)-C(17)	1.314(4)	C(5)-C(10)	1.423(4)	C(16)-C(18)	1.563(6)

C(11)-O(1)-C(2)	116.8(2)	C(14)-C(13)-C(16)	125.5(3)
C(15)-N(1)-C(11)	117.7(2)	C(12)-C(13)-C(16)	118.4(3)
C(2)-C(1)-C(9)	117.6(2)	F(2)-C(14)-C(13)	121.7(3)
C(2)-C(1)-C(1)#1	120.8(2)	F(2)-C(14)-C(15)	119.1(3)
C(9)-C(1)-C(1)#1	121.6(2)	C(13)-C(14)-C(15)	119.2(3)
C(1)-C(2)-C(3)	123.7(2)	N(1)-C(15)-F(3)	116.9(2)
C(1)-C(2)-O(1)	120.5(2)	N(1)-C(15)-C(14)	124.2(3)
C(3)-C(2)-O(1)	115.7(2)	F(3)-C(15)-C(14)	118.9(3)
C(4)-C(3)-C(2)	118.9(3)	F(4)-C(16)-C(17)	105.0(3)
C(3)-C(4)-C(10)	121.3(3)	F(4)-C(16)-C(13)	109.5(3)
C(6)-C(5)-C(10)	121.6(3)	C(17)-C(16)-C(13)	111.8(3)
C(5)-C(6)-C(7)	120.1(3)	F(4)-C(16)-C(18)	102.9(3)
C(8)-C(7)-C(6)	120.3(3)	C(17)-C(16)-C(18)	112.2(3)
C(7)-C(8)-C(9)	120.8(3)	C(13)-C(16)-C(18)	114.6(3)
C(8)-C(9)-C(10)	118.9(3)	F(7)-C(17)-F(5)	109.3(3)
C(8)-C(9)-C(1)	121.5(2)	F(7)-C(17)-F(6)	107.2(3)
C(10)-C(9)-C(1)	119.5(2)	F(5)-C(17)-F(6)	104.0(3)
C(4)-C(10)-C(5)	122.8(3)	F(7)-C(17)-C(16)	113.2(4)
C(4)-C(10)-C(9)	118.9(3)	F(5)-C(17)-C(16)	112.2(3)
C(5)-C(10)-C(9)	118.3(3)	F(6)-C(17)-C(16)	110.3(3)
N(1)-C(11)-O(1)	120.5(2)	F(10)-C(18)-F(8)	109.8(4)
N(1)-C(11)-C(12)	122.5(2)	F(10)-C(18)-F(9)	104.0(4)
O(1)-C(11)-C(12)	116.9(2)	F(8)-C(18)-F(9)	108.7(3)
F(1)-C(12)-C(13)	122.3(2)	F(10)-C(18)-C(16)	110.1(4)
F(1)-C(12)-C(11)	117.5(2)	F(8)-C(18)-C(16)	112.9(3)
C(13)-C(12)-C(11)	120.2(3)	F(9)-C(18)-C(16)	110.9(4)
C(14)-C(13)-C(12)	116.1(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 01srv017
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
O(1)	447(1)	3891(2)	2088(2)	21(1)
N(1)	1140(1)	2503(2)	2906(2)	21(1)
F(1)	751(1)	5262(2)	4017(2)	35(1)
F(2)	2175(1)	2437(2)	5744(2)	40(1)
F(3)	1813(1)	1169(2)	3701(2)	37(1)
F(4)	1201(1)	5240(3)	6180(2)	49(1)
F(4A)	2347(5)	4067(12)	6680(11)	9(3)
F(5)	1691(1)	6629(2)	5165(2)	47(1)
F(6)	2366(1)	5488(2)	5909(2)	46(1)
F(7)	2111(1)	6562(3)	7040(2)	54(1)
F(5A)	1927(10)	6160(20)	5118(16)	49(6)
F(6A)	1436(6)	6285(17)	6110(15)	30(4)
F(7A)	2307(11)	6200(30)	7140(20)	70(10)
F(8)	1699(1)	2792(2)	7231(2)	50(1)
F(9)	2405(1)	3868(2)	7614(2)	49(1)
F(10)	1856(1)	4622(4)	8144(3)	56(1)
F(9A)	1140(5)	4062(12)	6715(11)	11(3)
F(10A)	1690(8)	4480(20)	8050(20)	21(5)
C(1)	-63(1)	1980(2)	1860(2)	17(1)
C(2)	126(1)	2915(3)	1380(2)	19(1)
C(3)	-12(1)	3035(3)	178(2)	25(1)
C(4)	-358(1)	2189(3)	-571(3)	29(1)
C(5)	-934(1)	297(3)	-906(3)	36(1)
C(6)	-1125(2)	-666(4)	-481(3)	43(1)
C(7)	-961(1)	-813(3)	739(3)	38(1)
C(8)	-616(1)	35(3)	1500(3)	28(1)
C(9)	-409(1)	1051(3)	1080(2)	20(1)
C(10)	-567(1)	1182(3)	-152(2)	26(1)
C(11)	879(1)	3506(3)	3005(2)	19(1)
C(12)	1039(1)	4240(3)	4024(2)	24(1)
C(13)	1477(1)	3899(3)	5003(3)	27(1)
C(14)	1744(1)	2842(3)	4876(2)	29(1)
C(15)	1558(1)	2190(3)	3813(3)	25(1)
C(16)	1636(1)	4732(4)	6115(3)	32(1)
C(16A)	1848(10)	4290(30)	6260(20)	12(5)
C(17)	1945(1)	5874(3)	6076(3)	45(1)
C(18)	1895(2)	3972(5)	7288(3)	46(1)
C(18A)	1610(11)	3810(20)	7060(20)	12(5)

Table 6. Torsion angles [°] for 01srv017.

C(9)-C(1)-C(2)-C(3)	2.2(4)	F(1)-C(12)-C(13)-C(16)	-0.1(4)
C(1)#1-C(1)-C(2)-C(3)	-174.3(3)	C(11)-C(12)-C(13)-C(16)	-179.4(3)
C(9)-C(1)-C(2)-O(1)	177.0(2)	C(12)-C(13)-C(14)-F(2)	178.6(3)
C(1)#1-C(1)-C(2)-O(1)	0.5(4)	C(16)-C(13)-C(14)-F(2)	0.4(5)
C(11)-O(1)-C(2)-C(1)	56.6(3)	C(12)-C(13)-C(14)-C(15)	-0.9(4)
C(11)-O(1)-C(2)-C(3)	-128.1(3)	C(16)-C(13)-C(14)-C(15)	-179.1(3)
C(1)-C(2)-C(3)-C(4)	0.7(4)	C(11)-N(1)-C(15)-F(3)	179.4(2)
O(1)-C(2)-C(3)-C(4)	-174.4(3)	C(11)-N(1)-C(15)-C(14)	0.5(4)
C(2)-C(3)-C(4)-C(10)	-1.7(5)	F(2)-C(14)-C(15)-N(1)	180.0(3)
C(10)-C(5)-C(6)-C(7)	0.0(6)	C(13)-C(14)-C(15)-N(1)	-0.5(5)
C(5)-C(6)-C(7)-C(8)	1.4(6)	F(2)-C(14)-C(15)-F(3)	1.1(4)
C(6)-C(7)-C(8)-C(9)	-1.5(5)	C(13)-C(14)-C(15)-F(3)	-179.4(3)
C(7)-C(8)-C(9)-C(10)	0.2(5)	C(14)-C(13)-C(16)-F(4)	-150.4(3)
C(7)-C(8)-C(9)-C(1)	177.4(3)	C(12)-C(13)-C(16)-F(4)	31.4(4)
C(2)-C(1)-C(9)-C(8)	178.8(3)	C(14)-C(13)-C(16)-C(17)	93.6(4)
C(1)#1-C(1)-C(9)-C(8)	-4.7(4)	C(12)-C(13)-C(16)-C(17)	-84.5(4)
C(2)-C(1)-C(9)-C(10)	-4.1(4)	C(14)-C(13)-C(16)-C(18)	-35.4(5)
C(1)#1-C(1)-C(9)-C(10)	172.4(3)	C(12)-C(13)-C(16)-C(18)	146.4(3)
C(3)-C(4)-C(10)-C(5)	179.0(3)	F(4)-C(16)-C(17)-F(7)	65.1(4)
C(3)-C(4)-C(10)-C(9)	-0.3(5)	C(13)-C(16)-C(17)-F(7)	-176.3(3)
C(6)-C(5)-C(10)-C(4)	179.5(3)	C(18)-C(16)-C(17)-F(7)	-46.0(4)
C(6)-C(5)-C(10)-C(9)	-1.2(5)	F(4)-C(16)-C(17)-F(5)	-59.3(4)
C(8)-C(9)-C(10)-C(4)	-179.6(3)	C(13)-C(16)-C(17)-F(5)	59.3(4)
C(1)-C(9)-C(10)-C(4)	3.2(4)	C(18)-C(16)-C(17)-F(5)	-170.3(3)
C(8)-C(9)-C(10)-C(5)	1.1(4)	F(4)-C(16)-C(17)-F(6)	-174.8(3)
C(1)-C(9)-C(10)-C(5)	-176.1(3)	C(13)-C(16)-C(17)-F(6)	-56.2(4)
C(15)-N(1)-C(11)-O(1)	178.8(2)	C(18)-C(16)-C(17)-F(6)	74.2(4)
C(15)-N(1)-C(11)-C(12)	1.0(4)	F(4)-C(16)-C(18)-F(10)	-39.7(5)
C(2)-O(1)-C(11)-N(1)	37.6(3)	C(17)-C(16)-C(18)-F(10)	72.7(5)
C(2)-O(1)-C(11)-C(12)	-144.5(2)	C(13)-C(16)-C(18)-F(10)	-158.5(4)
N(1)-C(11)-C(12)-F(1)	178.3(2)	F(4)-C(16)-C(18)-F(8)	83.5(4)
O(1)-C(11)-C(12)-F(1)	0.3(4)	C(17)-C(16)-C(18)-F(8)	-164.2(3)
N(1)-C(11)-C(12)-C(13)	-2.4(4)	C(13)-C(16)-C(18)-F(8)	-35.3(5)
O(1)-C(11)-C(12)-C(13)	179.6(3)	F(4)-C(16)-C(18)-F(9)	-154.3(3)
F(1)-C(12)-C(13)-C(14)	-178.4(3)	C(17)-C(16)-C(18)-F(9)	-41.9(4)
C(11)-C(12)-C(13)-C(14)	2.3(4)	C(13)-C(16)-C(18)-F(9)	86.9(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 01srv017. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	20(1)	23(1)	1(1)	8(1)	-3(1)
N(1)	21(1)	25(1)	20(1)	-3(1)	11(1)	-2(1)
F(1)	37(1)	32(1)	36(1)	-12(1)	16(1)	3(1)
F(2)	27(1)	57(1)	26(1)	4(1)	2(1)	8(1)
F(3)	30(1)	41(1)	40(1)	-2(1)	14(1)	14(1)
F(4)	33(1)	77(2)	31(1)	-19(1)	9(1)	23(1)
F(5)	48(1)	28(1)	49(1)	-6(1)	4(1)	6(1)
F(6)	34(1)	39(1)	57(2)	-10(1)	11(1)	1(1)
F(7)	47(2)	49(2)	45(2)	-33(1)	-2(1)	0(1)
F(8)	59(1)	62(2)	34(1)	8(1)	24(1)	5(1)
F(9)	40(1)	58(2)	33(1)	-8(1)	-2(1)	20(1)
F(10)	48(2)	95(3)	21(1)	-15(1)	10(2)	17(2)
C(1)	18(1)	18(1)	16(1)	-1(1)	8(1)	2(1)
C(2)	17(1)	19(1)	19(1)	-2(1)	7(1)	0(1)
C(3)	25(1)	31(2)	21(1)	4(1)	13(1)	-4(1)
C(4)	29(2)	42(2)	16(1)	1(1)	11(1)	-6(1)
C(5)	39(2)	48(2)	25(2)	-17(1)	18(1)	-14(2)
C(6)	53(2)	48(2)	39(2)	-27(2)	29(2)	-28(2)
C(7)	53(2)	33(2)	42(2)	-13(2)	32(2)	-20(2)
C(8)	37(2)	24(2)	28(2)	-6(1)	20(1)	-7(1)
C(9)	26(1)	19(1)	22(1)	-3(1)	16(1)	0(1)
C(10)	28(1)	34(2)	19(1)	-7(1)	14(1)	-5(1)
C(11)	19(1)	22(1)	21(1)	-1(1)	12(1)	-4(1)
C(12)	27(1)	25(1)	24(1)	-6(1)	15(1)	-4(1)
C(13)	31(2)	30(2)	22(1)	-7(1)	12(1)	-8(1)
C(14)	21(1)	43(2)	20(1)	5(1)	5(1)	-4(1)
C(15)	21(1)	27(1)	28(2)	-1(1)	14(1)	3(1)
C(16)	28(2)	38(2)	25(2)	-8(2)	8(1)	11(2)
C(17)	44(2)	33(2)	39(2)	-18(2)	-3(2)	13(2)
C(18)	51(3)	63(3)	22(2)	-7(2)	12(2)	19(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 \times 10^3$) for 01srv017.

Atom	x	y	z	U(eq)
H(3)	157(13)	3720(30)	-20(30)	28(9)
H(4)	-445(16)	2280(40)	-1390(40)	57(12)
H(5)	-1031(14)	420(40)	-1770(30)	41(10)
H(6)	-1349(14)	-1280(40)	-960(30)	38(10)
H(7)	-1052(16)	-1490(40)	1080(30)	50(11)
H(8)	-518(14)	0(30)	2310(30)	34(9)

2) 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-[2,3,8,10,13,18-hexaaza-6,7,15,17-tetrafluoro-2,3,10,13-tetramethyl-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyloxy)tricyclo[12.3.1.0<4,9>]octadeca-1(18),4(9),5,7,14,16-hexaen-16-yloxy]octane (49)

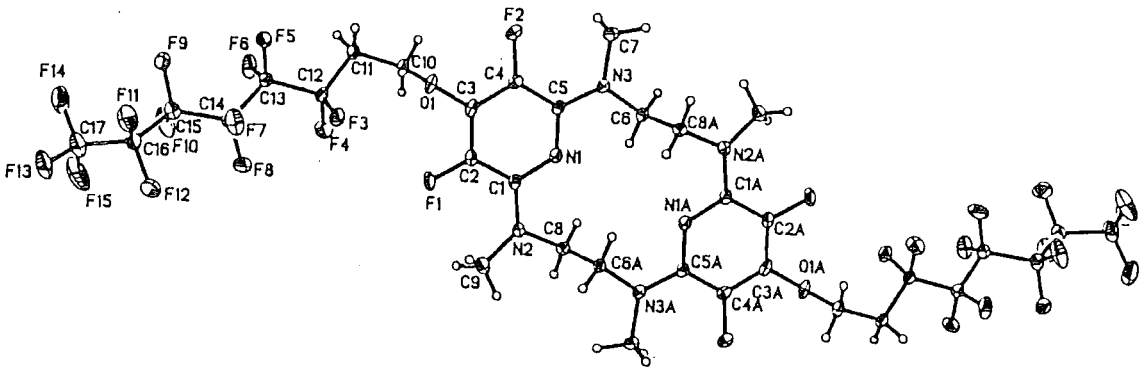

Table 1. Crystal data and structure refinement for 01srv003.

Identification code	s003	
Empirical formula	$C_{34}\ H_{28}\ F_{30}\ N_4\ O_2$	
Formula weight	1122.62	
Temperature	100.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.4855(4) Å	α= 75.596(2)°.
	b = 9.8445(6) Å	β= 81.248(3)°.
	c = 16.504(1) Å	γ = 87.719(3)°.
Volume	1008.74(11) Å^3	
Z	1	
Density (calculated)	1.848 Mg/m^3	
Absorption coefficient	0.212 mm^{-1}	
F(000)	560	
Crystal size	0.50 x 0.18 x 0.08 mm^3	
Theta range for data collection	2.14 to 30.40°.	
Index ranges	-8<=h<=9, -13<=k<=13, -23<=l<=23	
Reflections collected	11678	
Independent reflections	5497 [R(int) = 0.0376]	
Completeness to theta = 30.40°	90.2 %	
Absorption correction	None	
Max. and min. transmission	0.9833 and 0.9015	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5497 / 0 / 381	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0973	
R indices (all data)	R1 = 0.0711, wR2 = 0.1100	
Largest diff. peak and hole	0.421 and -0.286 e.Å^{-3}	

Table 3. Bond lengths [Å] and angles [°] for 01srv003.

O(1)-C(3)	1.378(2)	C(3)-C(4)	1.389(2)	C(14)-F(8)	1.332(2)
O(1)-C(10)	1.442(2)	C(4)-F(2)	1.365(2)	C(14)-F(7)	1.349(2)
N(1)-C(5)	1.345(2)	C(4)-C(5)	1.406(2)	C(14)-C(15)	1.560(3)
N(1)-C(1)	1.346(2)	C(6)-C(8)#1	1.534(3)	C(15)-F(9)	1.343(2)
N(2)-C(1)	1.377(2)	C(10)-C(11)	1.517(2)	C(15)-F(10)	1.344(2)
N(2)-C(9)	1.461(2)	C(11)-C(12)	1.518(2)	C(15)-C(16)	1.555(3)
N(2)-C(8)	1.464(2)	C(12)-F(3)	1.360(2)	C(16)-F(11)	1.343(2)
N(3)-C(5)	1.379(2)	C(12)-F(4)	1.363(2)	C(16)-F(12)	1.345(2)
N(3)-C(7)	1.462(2)	C(12)-C(13)	1.547(2)	C(16)-C(17)	1.544(3)
N(3)-C(6)	1.467(2)	C(13)-F(6)	1.345(2)	C(17)-F(15)	1.318(3)
C(1)-C(2)	1.405(2)	C(13)-F(5)	1.356(2)	C(17)-F(14)	1.322(3)
C(2)-F(1)	1.3641(19)	C(13)-C(14)	1.558(2)	C(17)-F(13)	1.335(2)
C(2)-C(3)	1.382(3)				

C(3)-O(1)-C(10)	113.83(13)	C(11)-C(12)-C(13)	112.23(14)
C(5)-N(1)-C(1)	123.07(15)	F(6)-C(13)-F(5)	108.23(15)
C(1)-N(2)-C(9)	122.77(15)	F(6)-C(13)-C(12)	108.34(14)
C(1)-N(2)-C(8)	119.22(14)	F(5)-C(13)-C(12)	107.47(13)
C(9)-N(2)-C(8)	116.55(15)	F(6)-C(13)-C(14)	109.03(14)
C(5)-N(3)-C(7)	122.99(15)	F(5)-C(13)-C(14)	107.03(14)
C(5)-N(3)-C(6)	119.75(15)	C(12)-C(13)-C(14)	116.47(15)
C(7)-N(3)-C(6)	115.65(14)	F(8)-C(14)-F(7)	108.57(16)
N(1)-C(1)-N(2)	116.61(15)	F(8)-C(14)-C(13)	109.74(15)
N(1)-C(1)-C(2)	119.11(16)	F(7)-C(14)-C(13)	108.43(15)
N(2)-C(1)-C(2)	124.28(15)	F(8)-C(14)-C(15)	108.64(15)
F(1)-C(2)-C(3)	117.84(15)	F(7)-C(14)-C(15)	108.10(15)
F(1)-C(2)-C(1)	122.45(16)	C(13)-C(14)-C(15)	113.25(15)
C(3)-C(2)-C(1)	119.67(15)	F(9)-C(15)-F(10)	108.55(17)
O(1)-C(3)-C(2)	120.31(15)	F(9)-C(15)-C(16)	108.15(16)
O(1)-C(3)-C(4)	120.14(16)	F(10)-C(15)-C(16)	108.00(15)
C(2)-C(3)-C(4)	119.54(15)	F(9)-C(15)-C(14)	109.37(15)
F(2)-C(4)-C(3)	117.00(15)	F(10)-C(15)-C(14)	108.55(16)
F(2)-C(4)-C(5)	123.36(15)	C(16)-C(15)-C(14)	114.09(16)
C(3)-C(4)-C(5)	119.62(16)	F(11)-C(16)-F(12)	108.21(17)
N(1)-C(5)-N(3)	116.22(15)	F(11)-C(16)-C(17)	107.62(17)
N(1)-C(5)-C(4)	118.93(15)	F(12)-C(16)-C(17)	108.02(17)
N(3)-C(5)-C(4)	124.81(16)	F(11)-C(16)-C(15)	108.69(16)
N(3)-C(6)-C(8)#1	110.59(15)	F(12)-C(16)-C(15)	109.38(16)
N(2)-C(8)-C(6)#1	113.54(15)	C(17)-C(16)-C(15)	114.74(17)
O(1)-C(10)-C(11)	108.06(14)	F(15)-C(17)-F(14)	110.0(2)
C(10)-C(11)-C(12)	113.93(15)	F(15)-C(17)-F(13)	107.96(18)
F(3)-C(12)-F(4)	106.76(14)	F(14)-C(17)-F(13)	108.04(19)
F(3)-C(12)-C(11)	112.22(14)	F(15)-C(17)-C(16)	111.19(19)
F(4)-C(12)-C(11)	110.28(14)	F(14)-C(17)-C(16)	110.80(18)
F(3)-C(12)-C(13)	107.43(14)	F(13)-C(17)-C(16)	108.75(18)
F(4)-C(12)-C(13)	107.66(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x-1,-y+2,-z+1

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 01srv003
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

Atom	x	y	z	U(eq)
O(1)	1885(2)	5537(1)	6081(1)	20(1)
N(1)	-2402(2)	8909(2)	5315(1)	16(1)
N(2)	-2859(2)	9575(2)	6582(1)	20(1)
N(3)	-2204(2)	8507(2)	3983(1)	20(1)
C(1)	-1886(3)	8718(2)	6095(1)	16(1)
C(2)	-396(3)	7692(2)	6358(1)	18(1)
C(3)	504(3)	6896(2)	5816(1)	17(1)
C(4)	-24(3)	7151(2)	5008(1)	17(1)
C(5)	-1511(3)	8190(2)	4758(1)	16(1)
C(6)	-3543(3)	9736(2)	3752(1)	16(1)
C(7)	-1295(3)	7892(2)	3289(1)	22(1)
C(8)	-4198(3)	10715(2)	6204(1)	18(1)
C(9)	-3015(3)	9223(2)	7503(1)	23(1)
C(10)	4015(3)	6300(2)	5968(1)	20(1)
C(11)	5253(3)	5131(2)	6465(1)	18(1)
C(12)	4763(3)	4929(2)	7417(1)	17(1)
C(13)	6361(3)	3957(2)	7890(1)	17(1)
C(14)	5819(3)	3487(2)	8871(1)	21(1)
C(15)	7746(3)	2933(2)	9319(1)	23(1)
C(16)	7178(3)	2054(2)	10246(1)	25(1)
C(17)	8963(4)	1886(3)	10785(1)	34(1)
F(1)	264(2)	7475(1)	7127(1)	24(1)
F(2)	989(2)	6380(1)	4486(1)	23(1)
F(3)	2838(2)	4368(1)	7735(1)	25(1)
F(4)	4787(2)	6186(1)	7622(1)	29(1)
F(5)	6533(2)	2776(1)	7601(1)	28(1)
F(6)	8223(2)	4604(1)	7686(1)	31(1)
F(7)	4401(2)	2447(1)	9069(1)	34(1)
F(8)	4986(2)	4557(1)	9168(1)	40(1)
F(9)	8926(2)	2131(2)	8879(1)	36(1)
F(10)	8888(2)	4037(1)	9330(1)	43(1)
F(11)	6608(2)	764(1)	10233(1)	36(1)
F(12)	5548(2)	2652(2)	10635(1)	40(1)
F(13)	8411(2)	921(2)	11506(1)	45(1)
F(14)	10691(2)	1454(2)	10387(1)	50(1)
F(15)	9311(3)	3070(2)	10977(1)	60(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 01srv003.

Atom	x	y	z	U(eq)
H(61)	-3520(30)	10350(20)	4136(12)	14(5)
H(62)	-2990(30)	10270(20)	3149(13)	17(5)
H(71)	100(40)	8250(20)	3059(14)	27(6)
H(72)	-1220(40)	6870(30)	3456(14)	28(6)
H(73)	-2160(40)	8150(20)	2849(15)	29(6)
H(81)	-3590(30)	11080(20)	5620(13)	18(5)
H(82)	-4110(30)	11470(20)	6511(13)	19(5)
H(91)	-3180(40)	8260(30)	7734(16)	40(7)
H(92)	-4180(50)	9650(30)	7725(18)	52(8)
H(93)	-1760(50)	9560(30)	7668(17)	50(8)
H(101)	4600(30)	6510(20)	5363(14)	23(6)
H(102)	4050(40)	7150(30)	6144(14)	28(6)
H(111)	6680(40)	5330(20)	6305(13)	20(5)
H(112)	5040(40)	4220(20)	6328(14)	29(6)

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 01srv003. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	13(1)	14(1)	32(1)	0(1)	-8(1)	2(1)
N(1)	14(1)	16(1)	17(1)	-3(1)	-2(1)	1(1)
N(2)	20(1)	24(1)	15(1)	-5(1)	-6(1)	5(1)
N(3)	19(1)	22(1)	19(1)	-7(1)	-4(1)	8(1)
C(1)	12(1)	18(1)	18(1)	-2(1)	-4(1)	-1(1)
C(2)	15(1)	19(1)	18(1)	-1(1)	-6(1)	0(1)
C(3)	11(1)	13(1)	25(1)	1(1)	-5(1)	0(1)
C(4)	13(1)	17(1)	21(1)	-5(1)	0(1)	1(1)
C(5)	12(1)	17(1)	18(1)	-2(1)	-1(1)	0(1)
C(6)	17(1)	15(1)	17(1)	-3(1)	-5(1)	3(1)
C(7)	23(1)	23(1)	19(1)	-8(1)	-2(1)	5(1)
C(8)	18(1)	18(1)	18(1)	-5(1)	-4(1)	2(1)
C(9)	27(1)	25(1)	18(1)	-5(1)	-6(1)	3(1)
C(10)	13(1)	21(1)	23(1)	1(1)	-4(1)	1(1)
C(11)	14(1)	19(1)	19(1)	-2(1)	-3(1)	3(1)
C(12)	15(1)	17(1)	20(1)	-5(1)	-3(1)	3(1)
C(13)	14(1)	19(1)	19(1)	-6(1)	-2(1)	1(1)
C(14)	21(1)	22(1)	19(1)	-5(1)	-4(1)	2(1)
C(15)	23(1)	25(1)	19(1)	-3(1)	-6(1)	-2(1)
C(16)	25(1)	29(1)	19(1)	-3(1)	-5(1)	1(1)
C(17)	35(1)	42(1)	22(1)	2(1)	-11(1)	-4(1)
F(1)	25(1)	26(1)	21(1)	-2(1)	-12(1)	4(1)
F(2)	22(1)	22(1)	27(1)	-9(1)	-3(1)	8(1)
F(3)	13(1)	35(1)	22(1)	-3(1)	-1(1)	0(1)
F(4)	44(1)	18(1)	31(1)	-10(1)	-12(1)	7(1)
F(5)	42(1)	24(1)	23(1)	-11(1)	-12(1)	14(1)
F(6)	17(1)	43(1)	27(1)	7(1)	-7(1)	-8(1)
F(7)	25(1)	42(1)	28(1)	7(1)	-6(1)	-13(1)
F(8)	59(1)	40(1)	23(1)	-15(1)	-9(1)	26(1)
F(9)	30(1)	52(1)	21(1)	-6(1)	-5(1)	19(1)
F(10)	50(1)	41(1)	35(1)	7(1)	-23(1)	-24(1)
F(11)	48(1)	26(1)	34(1)	2(1)	-15(1)	-9(1)
F(12)	40(1)	54(1)	20(1)	-5(1)	0(1)	15(1)
F(13)	42(1)	60(1)	23(1)	11(1)	-11(1)	-3(1)
F(14)	26(1)	82(1)	33(1)	6(1)	-8(1)	5(1)
F(15)	91(1)	56(1)	42(1)	-8(1)	-38(1)	-18(1)

Table 6. Torsion angles [°] for 01srv003.

C(5)-N(1)-C(1)-N(2)	177.06(16)	F(3)-C(12)-C(13)-F(5)	73.13(17)
C(5)-N(1)-C(1)-C(2)	-2.1(3)	F(4)-C(12)-C(13)-F(5)	-172.22(14)
C(9)-N(2)-C(1)-N(1)	159.38(17)	C(11)-C(12)-C(13)-F(5)	-50.69(19)
C(8)-N(2)-C(1)-N(1)	-6.3(2)	F(3)-C(12)-C(13)-C(14)	-46.8(2)
C(9)-N(2)-C(1)-C(2)	-21.5(3)	F(4)-C(12)-C(13)-C(14)	67.80(19)
C(8)-N(2)-C(1)-C(2)	172.80(16)	C(11)-C(12)-C(13)-C(14)	-170.67(15)
N(1)-C(1)-C(2)-F(1)	177.46(15)	F(6)-C(13)-C(14)-F(8)	82.97(19)
N(2)-C(1)-C(2)-F(1)	-1.6(3)	F(5)-C(13)-C(14)-F(8)	-160.18(15)
N(1)-C(1)-C(2)-C(3)	-0.2(3)	C(12)-C(13)-C(14)-F(8)	-40.0(2)
N(2)-C(1)-C(2)-C(3)	-179.35(17)	F(6)-C(13)-C(14)-F(7)	-155.59(15)
C(10)-O(1)-C(3)-C(2)	-86.6(2)	F(5)-C(13)-C(14)-F(7)	-41.73(19)
C(10)-O(1)-C(3)-C(4)	94.68(19)	C(12)-C(13)-C(14)-F(7)	78.49(19)
F(1)-C(2)-C(3)-O(1)	5.6(2)	F(6)-C(13)-C(14)-C(15)	-38.6(2)
C(1)-C(2)-C(3)-O(1)	-176.59(15)	F(5)-C(13)-C(14)-C(15)	78.24(18)
F(1)-C(2)-C(3)-C(4)	-175.70(15)	C(12)-C(13)-C(14)-C(15)	-161.54(15)
C(1)-C(2)-C(3)-C(4)	2.1(3)	F(8)-C(14)-C(15)-F(9)	-163.41(15)
O(1)-C(3)-C(4)-F(2)	-4.5(2)	F(7)-C(14)-C(15)-F(9)	78.95(19)
C(2)-C(3)-C(4)-F(2)	176.85(15)	C(13)-C(14)-C(15)-F(9)	-41.2(2)
O(1)-C(3)-C(4)-C(5)	176.96(15)	F(8)-C(14)-C(15)-F(10)	-45.1(2)
C(2)-C(3)-C(4)-C(5)	-1.7(3)	F(7)-C(14)-C(15)-F(10)	-162.79(15)
C(1)-N(1)-C(5)-N(3)	-179.84(16)	C(13)-C(14)-C(15)-F(10)	77.1(2)
C(1)-N(1)-C(5)-C(4)	2.5(3)	F(8)-C(14)-C(15)-C(16)	75.3(2)
C(7)-N(3)-C(5)-N(1)	175.63(17)	F(7)-C(14)-C(15)-C(16)	-42.3(2)
C(6)-N(3)-C(5)-N(1)	10.7(2)	C(13)-C(14)-C(15)-C(16)	-162.47(16)
C(7)-N(3)-C(5)-C(4)	-6.8(3)	F(9)-C(15)-C(16)-F(11)	-44.4(2)
C(6)-N(3)-C(5)-C(4)	-171.73(17)	F(10)-C(15)-C(16)-F(11)	-161.67(16)
F(2)-C(4)-C(5)-N(1)	-178.99(15)	C(14)-C(15)-C(16)-F(11)	77.6(2)
C(3)-C(4)-C(5)-N(1)	-0.5(3)	F(9)-C(15)-C(16)-F(12)	-162.32(16)
F(2)-C(4)-C(5)-N(3)	3.5(3)	F(10)-C(15)-C(16)-F(12)	80.4(2)
C(3)-C(4)-C(5)-N(3)	-177.97(17)	C(14)-C(15)-C(16)-F(12)	-40.4(2)
C(5)-N(3)-C(6)-C(8)#1	-106.02(18)	F(9)-C(15)-C(16)-C(17)	76.1(2)
C(7)-N(3)-C(6)-C(8)#1	88.02(19)	F(10)-C(15)-C(16)-C(17)	-41.2(2)
C(1)-N(2)-C(8)-C(6)#1	86.6(2)	C(14)-C(15)-C(16)-C(17)	-161.93(18)
C(9)-N(2)-C(8)-C(6)#1	-80.0(2)	F(11)-C(16)-C(17)-F(15)	-166.69(18)
C(3)-O(1)-C(10)-C(11)	166.79(15)	F(12)-C(16)-C(17)-F(15)	-50.1(2)
O(1)-C(10)-C(11)-C(12)	-72.0(2)	C(15)-C(16)-C(17)-F(15)	72.2(2)
C(10)-C(11)-C(12)-F(3)	71.0(2)	F(11)-C(16)-C(17)-F(14)	70.6(2)
C(10)-C(11)-C(12)-F(4)	-47.9(2)	F(12)-C(16)-C(17)-F(14)	-172.73(17)
C(10)-C(11)-C(12)-C(13)	-167.94(15)	C(15)-C(16)-C(17)-F(14)	-50.5(3)
F(3)-C(12)-C(13)-F(6)	-170.13(14)	F(11)-C(16)-C(17)-F(13)	-48.0(2)
F(4)-C(12)-C(13)-F(6)	-55.48(18)	F(12)-C(16)-C(17)-F(13)	68.7(2)
C(11)-C(12)-C(13)-F(6)	66.05(19)	C(15)-C(16)-C(17)-F(13)	-169.06(18)

Symmetry transformations used to generate equivalent atoms: #1 -x-1,-y+2,-z+1

3) 3-fluoro-6-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-2,4,5-tris(trifluoromethyl)benzenecarbonitrile (72)

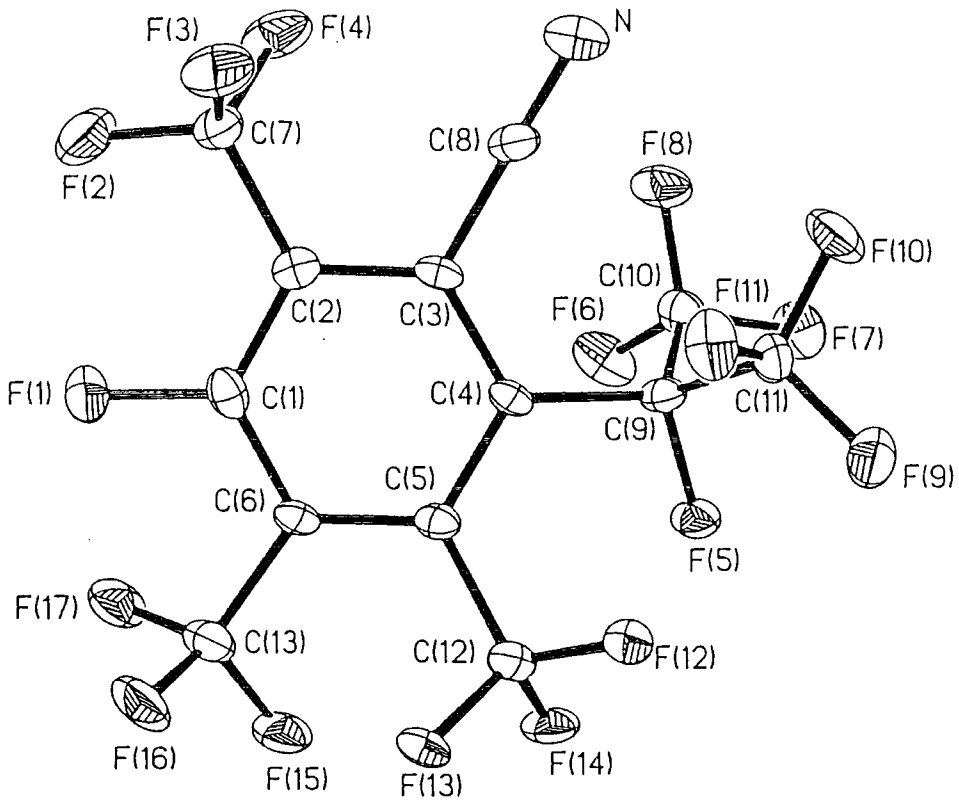

Table 1. Crystal data and structure refinement for 00srv035.

Identification code	
Empirical formula	$C_{13}F_{17}N$
Formula weight	493.14
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	a = 9.542(1) Å, α = 90°
	b = 9.419(5) Å, β = 103.46(1)°
	c = 17.456(3) Å, γ = 90°
Volume	1525.8(9) Å^3
Z	4
Density (calculated)	2.147 g/cm^3
Absorption coefficient	0.274 mm^{-1}
F(000)	952
Crystal size	0.55 x 0.08 x 0.02 mm^3
θ range for data collection	2.2 to 27.5°.
Index ranges	$-12 \le h \le 12, -12 \le k \le 12, -22 \le l \le 22$
Reflections collected	10721
Independent reflections	3503 [R(int) = 0.106]
Reflections with $I > 2\sigma(I)$	1974
Completeness to θ = 27.5°	99.8 %
Absorption correction	None
Max. and min. transmission	0.9945 and 0.8640
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3503 / 0 / 280
Largest final shift/e.s.d. ratio	0.000
Goodness-of-fit on F^2	1.025
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0575, wR_2 = 0.1089
R indices (all data)	R_1 = 0.1279, wR_2 = 0.1353
Largest diff. peak and hole	0.339 and -0.351 e.Å^{-3}

Table 3. Bond lengths [Å] and angles [°] for 00srv055.

F(1)-C(1)	1.338(4)	F(17)-C(13)	1.331(5)
F(2)-C(7)	1.324(4)	N-C(8)	1.149(5)
F(3)-C(7)	1.328(4)	C(1)-C(2)	1.386(5)
F(4)-C(7)	1.337(4)	C(1)-C(6)	1.389(5)
F(5)-C(9)	1.379(4)	C(2)-C(3)	1.405(5)
F(6)-C(10)	1.326(5)	C(2)-C(7)	1.523(5)
F(7)-C(10)	1.332(5)	C(3)-C(4)	1.410(5)
F(8)-C(10)	1.326(4)	C(3)-C(8)	1.445(5)
F(9)-C(11)	1.318(4)	C(4)-C(5)	1.407(5)
F(10)-C(11)	1.343(4)	C(4)-C(9)	1.542(5)
F(11)-C(11)	1.328(4)	C(5)-C(6)	1.402(5)
F(12)-C(12)	1.337(4)	C(5)-C(12)	1.545(5)
F(13)-C(12)	1.343(4)	C(6)-C(13)	1.533(5)
F(14)-C(12)	1.334(4)	C(9)-C(10)	1.561(5)
F(15)-C(13)	1.340(5)	C(9)-C(11)	1.581(5)
F(16)-C(13)	1.339(4)		

F(1)-C(1)-C(2)	119.2(3)	C(5)-C(6)-C(13)	124.0(3)
F(1)-C(1)-C(6)	118.3(3)	F(2)-C(7)-F(3)	107.9(3)
C(2)-C(1)-C(6)	122.4(3)	F(2)-C(7)-F(4)	106.0(3)
C(1)-C(2)-C(3)	117.6(3)	F(3)-C(7)-F(4)	107.4(3)
C(1)-C(2)-C(7)	122.1(3)	F(2)-C(7)-C(2)	113.0(3)
C(3)-C(2)-C(7)	120.3(3)	F(3)-C(7)-C(2)	111.5(3)
C(2)-C(3)-C(4)	121.3(3)	F(4)-C(7)-C(2)	110.6(3)
C(2)-C(3)-C(8)	117.6(3)	N-C(8)-C(3)	174.4(4)
C(4)-C(3)-C(8)	120.6(3)	F(5)-C(9)-C(4)	109.0(3)
C(5)-C(4)-C(3)	118.7(3)	F(5)-C(9)-C(10)	99.5(3)
C(5)-C(4)-C(9)	120.9(3)	C(4)-C(9)-C(10)	113.3(3)
C(3)-C(4)-C(9)	120.3(3)	F(5)-C(9)-C(11)	106.6(3)
C(6)-C(5)-C(4)	119.2(3)	C(4)-C(9)-C(11)	113.7(3)
C(6)-C(5)-C(12)	118.7(3)	C(10)-C(9)-C(11)	113.4(3)
C(4)-C(5)-C(12)	120.6(3)	F(8)-C(10)-F(6)	107.9(3)
C(1)-C(6)-C(5)	119.5(3)	F(8)-C(10)-F(7)	108.2(3)
C(1)-C(6)-C(13)	116.5(3)	F(6)-C(10)-F(7)	108.1(3)

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^4$) for 00srv055. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	5(2)	2198(2)	402(1)	295(5)
F(2)	-1395(3)	4289(3)	644(2)	453(7)
F(3)	-544(2)	4634(2)	1879(1)	330(6)
F(4)	-287(3)	6210(2)	1033(2)	379(6)
F(5)	6278(2)	4431(2)	1445(1)	247(5)
F(6)	4826(3)	6219(2)	456(1)	343(6)
F(7)	6437(2)	7132(2)	1398(2)	363(6)
F(8)	4183(2)	7475(2)	1340(1)	314(6)
F(9)	7056(2)	4894(2)	2861(1)	332(6)
F(10)	5644(3)	6689(2)	2811(1)	352(6)
F(11)	4884(2)	4594(2)	2988(1)	297(5)
F(12)	5879(2)	2270(2)	2128(1)	230(5)
F(13)	4727(2)	556(2)	1473(1)	270(5)
F(14)	6071(2)	1886(2)	931(1)	266(5)
F(15)	3691(3)	630(2)	16(1)	348(6)
F(16)	2104(3)	-262(2)	596(2)	380(6)
F(17)	1453(3)	1025(2)	-449(1)	354(6)
N	2327(4)	6948(3)	2402(2)	303(8)
C(1)	1224(4)	2883(4)	732(2)	201(8)
C(2)	1146(4)	4155(4)	1118(2)	171(8)
C(3)	2450(4)	4827(3)	1475(2)	162(8)
C(4)	3789(4)	4234(3)	1440(2)	151(7)
C(5)	3818(4)	2856(4)	1133(2)	169(8)
C(6)	2527(4)	2237(3)	719(2)	172(8)
C(7)	-287(4)	4813(4)	1170(2)	223(8)
C(8)	2380(4)	6051(4)	1964(2)	209(8)
C(9)	5182(4)	5116(4)	1689(2)	191(8)
C(10)	5138(4)	6530(4)	1218(2)	267(9)
C(11)	5710(4)	5318(4)	2611(2)	238(9)
C(12)	5157(4)	1899(4)	1405(2)	214(8)
C(13)	2446(5)	883(4)	222(2)	276(9)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 00srv055. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + \ldots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(1)	23(1)	27(1)	36(1)	-4(1)	1(1)	-6(1)
F(2)	21(1)	66(2)	46(2)	-24(1)	1(1)	8(1)
F(3)	35(1)	37(1)	33(1)	2(1)	20(1)	8(1)
F(4)	34(1)	25(1)	60(2)	16(1)	20(1)	15(1)
F(5)	20(1)	20(1)	38(1)	-4(1)	14(1)	0(1)
F(6)	57(2)	22(1)	27(1)	4(1)	16(1)	-4(1)
F(7)	35(1)	21(1)	55(2)	4(1)	15(1)	-12(1)
F(8)	39(1)	14(1)	45(1)	4(1)	17(1)	5(1)
F(9)	25(1)	32(1)	39(1)	-1(1)	-1(1)	-2(1)
F(10)	48(2)	20(1)	35(1)	-11(1)	4(1)	0(1)
F(11)	31(1)	36(1)	23(1)	1(1)	6(1)	-10(1)
F(12)	24(1)	18(1)	26(1)	-1(1)	3(1)	2(1)
F(13)	31(1)	9(1)	40(1)	1(1)	5(1)	2(1)
F(14)	26(1)	23(1)	35(1)	-3(1)	14(1)	8(1)
F(15)	40(1)	27(1)	36(1)	-13(1)	7(1)	9(1)
F(16)	47(2)	13(1)	49(2)	0(1)	-1(1)	-4(1)
F(17)	43(2)	26(1)	31(1)	-11(1)	-6(1)	5(1)
N	35(2)	23(2)	34(2)	-5(2)	12(2)	6(2)
C(1)	24(2)	17(2)	18(2)	2(2)	2(2)	-5(2)
C(2)	19(2)	19(2)	15(2)	4(2)	8(2)	2(2)
C(3)	24(2)	10(2)	17(2)	1(1)	9(2)	3(2)
C(4)	23(2)	9(2)	14(2)	1(1)	5(2)	0(1)
C(5)	20(2)	15(2)	19(2)	-1(2)	10(2)	1(2)
C(6)	23(2)	10(2)	19(2)	2(1)	5(2)	3(2)
C(7)	19(2)	24(2)	25(2)	-1(2)	8(2)	3(2)
C(8)	19(2)	18(2)	27(2)	1(2)	9(2)	5(2)
C(9)	17(2)	16(2)	27(2)	1(2)	11(2)	3(2)
C(10)	29(2)	19(2)	35(2)	-1(2)	13(2)	-6(2)
C(11)	19(2)	18(2)	31(2)	-2(2)	0(2)	-3(2)
C(12)	23(2)	14(2)	27(2)	-1(2)	6(2)	2(2)
C(13)	32(2)	17(2)	32(2)	-4(2)	3(2)	3(2)

F(8)-C(10)-C(9)	115.0(3)	F(12)-C(12)-F(13)	105.2(3)
F(6)-C(10)-C(9)	108.2(3)	F(14)-C(12)-C(5)	115.3(3)
F(7)-C(10)-C(9)	109.2(3)	F(12)-C(12)-C(5)	110.2(3)
F(9)-C(11)-F(11)	109.0(3)	F(13)-C(12)-C(5)	109.2(3)
F(9)-C(11)-F(10)	107.8(3)	F(17)-C(13)-F(16)	107.8(3)
F(11)-C(11)-F(10)	107.1(3)	F(17)-C(13)-F(15)	106.0(3)
F(9)-C(11)-C(9)	110.9(3)	F(16)-C(13)-F(15)	108.6(3)
F(11)-C(11)-C(9)	111.0(3)	F(17)-C(13)-C(6)	110.2(3)
F(10)-C(11)-C(9)	110.9(3)	F(16)-C(13)-C(6)	112.3(3)
F(14)-C(12)-F(12)	108.6(3)	F(15)-C(13)-C(6)	111.7(3)
F(14)-C(12)-F(13)	107.7(3)		

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